NEW YORK UNIVERSITY

College of Engineering

RESEARCH DIVISION

University Heights, New York 53, N. Y.



# DEVELOPMENT OF IMPROVED TITANIUM ORGANIC COMPOUNDS FOR USE AS HYDRAULIC FLUIDS

December 14, 1962

Prepared under Navy, Bureau of Naval Weapons
Contract NOw 62-0647-d

TECHNICAL REPORT NO. 3.
Covering the period
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ABSTRACT

In this report period special effort was directed to the question of the fire safety of the experimental fluid, and how far this can be influenced and evaluated. The ASTM method of determining the flash and flame points by heating a sample to a high enough temperature to cause the flash and flame effect does not express the safety conditions of contact with open flames when the fluid itself is held below the high ranges of 560°F.-600°F. such as are found for these materials.

The synthesis work of this period has been directed at producing fluids with as-far-as-possible complete removal of low boiling cuts, so as to decrease short flashes of low cuts below the flame point. Also, work has been directed at increasing the self extinguishing properties after a short burning has taken place by the incorporation of phosphorus, halogen, or nitrogen, or combinations of these. The work is continuing.

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## SUMMARY

In this Report No. 3 efforts have been directed to improving the fire safety of the products which are here-under development. The standard ASTM test for the flash point and the fire point is limited to a heating of the fluid to high enough temperature ranges to cause, in contact with an open flame, a short flash, or continuous burning, of the fluid. For most conventional fluids, this test might be satisfactory; but the fluids developed under this project have, after removal of their low distillation cuts, a boiling range of about 570°F. at 2-3 mm. Hg. pressure, flash points around 550°F. and flame points close to 600°F. and require additional methods.

The ASTM test does not consider at what temperature the fluid will ignite in contact with locally overhot metals, at what temperature it will self-ignite, amd how it will behave when in contact with an open flame when it is not already at such high temperatures as indicated.

In SECTION A, the combustion behavior of the test fluids is studied by dropping the fluids on molten metal at temperature up to 1500°F. without an ignition taking place. If, however, flint sparks are released in the evaporating vapours of the fluid at that moment, the vapours will ignite.

Further-on is studied at what temperature the fluids in an open cup inside of a muffle oven will ignite. It is possible that hereby the vapours contact the heating elements of the muffle oven and so cause the ignition; but the results show that under these conditions the fluids do not ignite below 900° / 950°F. This might indicate that they do not give off vapours which might ignite in contact with the heating element.

Finally Section A shows a test whereby the test fluid is first brought to certain temperatures, and then is determined how long it will take before the hottest part of an open bunsen burner will cause a flash or fire which will not be self-extinguishing within a period of 5 seconds. FIGURE 1 shows an improvement of this characteristic by the effect of the benzyl alcohol modification of the experimental fluids of this development.

The Sections which follow give data on the production of the hydraulic fluid product in such a manner that it is obtained in a form in which it is free enough from non-complexed matter, or from "low cuts", to produce desirable fire characteristics, and with simultaneously such properties of oxidation-reduction test resistance and of hydrolytic stability and wear-test properties as will fulfil the requirements of this fluid.

SECTIONS B and C give data on the development of the product by reacting tetra isopropyl titanate, and other tetra alkyl titanates, with basic zinc octoate, with the use of titanium tetra chloride as catalyst.

In SECTION D water is added to the reaction; and the properties of these products, and of the earlier product made with aluminum chloride as catalyst, are being studied and evaluated. The benzyl alcohol modification is a part of each study.

In SECTION E the introduction of phosphorus into these products is being studied, using aliphatic organo phosphates, or mixtures of aliphatic and aromatic organo phosphates, or using an organo phosphoric acid.

In SECTION F chlorine groups are introduced either alone or chlorine is introduced besides phosphorus, and in subsequent periods nitrogen also is introduced in various forms. Also an ultimate, future aim is kept in mind to explore the reasons for the burning properties of a fluid.

In SECTION G the product is reacted with a tetra alkyl tin, instead of the tetra alkyl silane used earlier in this development. This is continuing. Other tetra alkyl silicones are being considered for future work, as well as organo derivatives of other metals such as boron and others.

In SECTION H a new preparation of cerium 2-ethyl hexanoate inhibiting treatment of Silicone Fluid 510 is reported. It is shown by emission spectroscopy that the cerium component becomes a part of the inhibited fluid and can not be removed by filtration in a molecular sieve.

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The work reported herein has been performed in Research Building No. 3 of the Research Division, College of Engineering, New York University, located at 233 Fordham Landing Road, New York (68) New York, under the direction of Dr. Max Kronstein, Senior Research Scientist. The following members of the research staff have participated in the work:

| | |
|---|---|
| Edward I. Stiefel | Research Aide |
| Robert A. Sierra | Research Aide |
| Jeannette Grace Musco, B.S. | Research Aide |
| Michael R. Carroad, B.Ch.E. | Research Aide |
| William Kapfer, Ph. D. | Chemical Engineer |
| Marion W. Kronstein, A. B. | Assistant Res. Scientist. |

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## SECTION A. EVALUATION OF THE FIRE SENSIBILITY OF THE EXPERIMENTAL FLUIDS.

### INTRODUCTION

Among the characteristics which it is desirable to know about, with respect to hydraulic fluids, is - besides their behavior at elevated temperatures - under what conditions they will flame , or catch fire, and continue to burn afterwards. In preceding reports of this project the flash point and flame point determinations have been made according to the Open Cup Method only. The results with this method had shown flash and flame points between 550°F. and 600°F. (This is considerably higher than commercially available organic fluids.) This test method, however, is not conclusive because according to this method the fluid is heated quite rapidly to a high temperature and the flame is then moved over the fluid. Hereby it measures primarily the conditions under which fumes are being given off, which can then be combusted by the open flame.

As applied to the aims of this project, it would require that the fluid in the hydraulic system would be heated to very high temperatures before contact is made with the flame; and such temperatures would not be expected to occur in the hydraulic system without other very serious fire causes already taking place. It was of interest, therefore, to use in addition a number of different test conditions in comparing the behavior of different fluids, and in particular, in comparing the different experimental fluids of this development in order to give additional guidance for influencing further developments.

### 1. COMBUSTION OF FLUID IN A HOT MUFFLE OVEN.

One of the questions studied was at what temperature will the fluid turn into flames, when it is in areas which are hot from reasons other than open flames?

In earlier projectsof this group, standard self-combustion tests have been reported, and the results were in very high temperature ranges. In the present study a simpler, but very interesting, test was made, as shown in TABLE 101. Hereby, several test fluids were studied by inserting them in an open crucible and transferring them

into a heated muffle oven, where the temperature was indicated on the oven thermometer. In the upper part of Table 101, the temperature of the oven containing the crucible was increased until the fluid started to burn. In the lower part of Table 101, the oven temperature was kept constant and the sample was inserted in a space of constant temperature for 60 seconds. When it was not ignited, it was taken out. The oven was heated to a higher temperature and then the sample was tested at the higher temperature until the fluid began to burn within 60 seconds.

The results in the case of the tetraisopropyl titanate/zinc octoate complex fluid and its modifications were, in the first test method, between 860°F. and 950°F.; in the second test method, between 900°F. and 950°F. At this temperature it is to be considered that hereby some vapors might have been given off which ignited in contact with the much hotter heating elements of the oven. It is interesting that in this Table 101 product T 42-111, whereby phosphate groups had been introduced into the system, burned at a lower temperature than the specimen without the phosphate components. What is still to be studied is whether or not this compound may still contain some "low cut" material which causes this earlier ignition.

2. COMBUSTION OF THE FLUID IN SUDDEN CONTACT WITH VERY HOT SURFACES.

A second study referred to what would occur if the fluids were suddenly in contact with very hot metal surfaces, such as an over heated metal part in an operating system of an aircraft. To test this an iron container was filled with a matal, zinc. (In future tests tin might be more suitable because of its higher evaporation temperature.) The container and zinc were placed in a muffle oven and the oven temperature was increased above the melting temperature of the zinc. That means that the molten zinc surface was at the oven temperature, as indicated on the temperature indicator of the muffle oven. At certain temperature levels a few drops of each test fluid were suddenly dropped on the metal surface. This means that the fluid was suddenly brought in contact with the molten zinc; and an observation was made when a flame formation could be detected. TABLE 102 lists results only at 1200°F. to 1500°F. . Lower temperatures were omitted in the table since no flame was observed in any of the lower temperature

(Continued on page 8.)

TABLE 101.

AUTO-IGNITION TESTS IN A MUFFLE OVEN

T 43 - 14

THE MATERIAL WAS KEPT IN AN OPEN CRUCIBLE AND INSERTED IN A"BLUE M"MUFFLE FURNACE SET ON"MEDIUM".

SETTING OF CONTROL : 6

THE PRODUCT BETWEEN TETRA ISOPROPYL TITANATE AND ZINCOCTOATE WITH ALUMINUM CHLORIDE CATALYST CAUGHT FIRE AT 920°F.

THE BENZYLALCOHOL MODIFICATION OF THE SAME REACTION ,MADE WITH TITANIUM TETRA CHLORIDE CATALYST ..... AT 860°F.

THE PRODUCT BETWEEN TRI OCTYL PHOSPHATE AND TRICRESYLPHOSPHATE AND TETRA ISOPROPYL TITANATE ( T 42-110) REACTED WITH ZINCOCTOATE AS T 42-111 ..... AT 620°F.

AND THE PRODUCT BEWEEN ZINCOCTOATE 18% AND TETRAISOPROPYL TITANATE WITH $TiCl_4$ ( T 42- 111 ) ..... AT 950°F.

REPEAT TESTS : OVEN KEPT AT CONSTANT TEMPERATURE. SAMPLE IN CRUCIBLE PLACED IN OVEN FOR 60 SECONDS .REPEATED UNTIL AUTOIGNITION OCCURS AT A SET TEMPERATURE WITHIN 60 SECONDS ( T 40 -95)

PRODUCT MADE WITH $TiCl_4$ AS CATALYST: AT 850°F. NO FLAME.
AT 900°F.FLAMES WITHIN 60 SECONDS.

SAME PRODUCT , BUT MODIFIED WITH BENZYLALCOHOL: AT 900°F. NO FLAME.
AT 950°F. FLAMES WITHIN 60 SECONDS.

PRODUCT MADE WITH $AlCl_3$ AS CATALYST ... AT 850°F. NO FLAME.
AT 900°F. FLAMES WITHIN 60 SEC.

TABLE 102.

STUDYING THE INFLAMMABILITY OF SOME OF THE PRODUCTS OF THIS DEVELOPMENT IN RESPECT TO THEIR COMBUSTION IN CONTACT WITH MOLTEN METAL.

T 40 -93

AS METAL, ZINC WAS SELECTED .(IN FUTURE TESTS TIN MIGHT BE USED BECAUSE OF ITS HIGHER EVAPORATING TEMPERATURE ).

THE ZINC WAS MOLTEN IN AN IRON CONTAINER. THE SURFACE WAS SKIMMED WITH A SPATULA BEFORE EACH TEST.

THE SYSTEM WAS BROUGHT TO A GIVEN TEMPERATURE BY HOLDING IT IN A TEMPERATURE REGULATED MUFFLE OVEN, READING THE OVEN TEMPERATURE ON THE INDICATOR OF THE OVEN.

A FEW DROPS OF THE TEST MATERIAL WERE DROPPED ON THE MOLTEN ZINC. IF IT FLAMES NO FURTHER TEST WAS MADE. IF NO FLAME RESULTED, THE TEST WAS REPEATED BUT IN ADDITION A SPARK FROM A FLINT LIGHTER WERE AIMED INTO THE EVAPORATING MATERIAL. ALL DATA WERE REPEATED TWICE.

| MATERIAL | TEMPERATURE INDICATED AS OVEN TEMPERATURE OR AS ZINC TEMPERATURE : | BURNS WITHOUT ADDITIONAL SPARKING | BURNS WITH SPARKING |
|---|---|---|---|
| PRODUCT TPT/ ZINCOCTOATE (WITH $AlCl_3$ CATALYST) | 1200° F. | NO | YES |
| | 1300° F. | NO | YES |
| | 1500° F. | NO | YES |
| PRODUCT OF TRIOCTYLPHOSPHATE & TRICRESYLPHOS - PHATE & TPT--REAC- TED WITH ZINCOCTOATE T 42-111 | 1300° F. | NO | YES |
| SILICONE FLUID INHIBITED ( 510) | 1200° F. | YES | YES |

(Continued from page 5.)

ranges. At 1500°F. the TPT/zinc octoate product did not cause a flame.

The reason that the tests were not continued at still higher levels was that at that temperature the zinc and the iron pot underwent some form of alloying, and a leak developed. This resulted in some of the zinc vaporizing and oxidizing. In future tests other metals than zinc will be used.

In the second test group of TABLE 102 the test material was sparked at the indicated temperature, using a flint sparker at the same time that the specimen was set on the hot surface. All the specimens were affected by the sparking. This is not necessarily due to the vapors of the fluid itself; it might indicate that at these temperatures the vapors represent a decomposition product of the fluids, and that these decomposition products can be influenced by the sparks. It is noted in this Table 102 that the inhibited Silicone Fluid 510 did burn when dropped on a surface at 1200°F.

3. A STUDY OF THE LENGTH OF CONTACT WITH AN OPEN FLAME WHICH CAUSES A FLAME FORMATION WHICH IS BEING SUSTAINED FOR 5 SECONDS.

In this study it is being explored how long a fluid can be in direct contact with a flame before it will burn for 5 seconds without self extinguishing before the end of that 5 second period.

In these tests the fluids are at different temperatures at the start of the test. They are placed in direct contact with the hottest area of the bunsenburner, exposing the burner at an angle of 60 degrees to the horizontal. Hereby, when a material is combustible it will begin to burn immediately or within a few seconds. The fact that the tetra isopropyl titanate/zinc octoate fluid complexes, when they are at room temperature or up to around 200/300°F., can be in contact with the open flame for considerable lengths of time before starting a 5 seconds burning period, indicates that they are of limited combustibility. Above this temperature range, that means, when approaching their flash points under the ASTM method, the period of direct contact is shorter, but it is still above 5 seconds direct flame exposure when the fluid itself is at temperatures up to around 450°F., and for the benzyl alcohol-modified product even up to 482°F. Immediate burning for 5 seconds occurs on the product when the fluid has

a temperature of 526°F. before contact with the flame is made, and at 572°F. for the benzyl alcohol modification. These data are shown in TABLE 103. Data on some other materials are given in TABLE 104. FIGURE 1 shows graphically the relationship between the time of contact with the bunsenburner flame and the temperature of two test fluids, before reaching a 5-second burning time of the fluids: Hereby A shows the reaction product between the tetraisopropyl titanate and zinc octoate with $TiCl_4$ catalyst; while B shows the benzyl alcohol modification of the same material. It is interesting to note here that the alcohol-modification gives a considerably smoother slope of the curve.

In new work a study is being made of the elapsed time between the start of the burning at a given temperature and the moment of self extinguishing after the open flame has been removed.

Also a study is being made on the introduction of such groups as phosphorus, or of a halogen, or of a combination of both, or the introduction of $NO_2$ or of $NH_2$ groups, with respect to the rate of self combustibility of the resulting product.

- - - -

TABLE 103.

A NEW TEST FOR THE DETERMINATION OF THE LENGTH OF TIME WHICH IS REQUIRED IN CONTACT WITH THE HOTTEST AREA OF THE BUNSENBURNER WITH THE TEST FLUID T 43-7 IN ORDER TO CAUSE A BURNING FOR FIVE SECONDS (WITHOUT SELF EXTINGUISHING BEFORE THAT TIME PERIOD ).

TEST FLUID USED: THE REACTION PRODUCT BETWEEN TETRA ISOPROPYL TITANATE AND BASIC ZINCOCTOATE 18% ZINC WITH $TiCl_4$ CATALYST ( T 43-7)

EXPOSED IN AN OPEN COVER FOR A CRUCIBLE : DIAMETER 35 mm.
DEPTH ... 5 mm.
WHICH IS FILLED WITH THE TEST FLUID.

THE HOTTEST PART OF THE FLAME OF THE BUNSENBURNER IS SET AGAINST THE SURFACE OF THE FLUID AT AN ANGLE OF 60 DEGREES( FROM THE HORIZONTAL ).

| AT A TEMPERATURE OF THE FLUID ( OBTAINED BEFORE FLAME TEST ) | | TIME REQUIRED TO OBTAIN A 5 SECOND BURNING TIME(IN SEC.) | COMMENT |
|---|---|---|---|
| R.T. 27°C .( 80°F.) | | 80 seconds | FLASHES ONLY |
| 50°C. | 122°F. | 47 sec 43 sec.(2 TESTS) | FLASHES |
| 75 | 167°F. | 50 | BURNS 5 SECONDS |
| 100 | 212°F. | 28 | |
| 125 | 257°F. | 20 | |
| 150 | 302°F. | 12 | |
| 175 | 347°F. | 9 | |
| 200 | 392°F. | 7 | |
| 225 | 436°F. | 7 | |
| 250 | 482°F. | 5 | |
| 275 | 526°F. | 0 | BURNS ON CONTACT WITH THE FLAME |

(TABLE CONTINUED )

TABLE 103 ( CONTINUED )

DETERMINATION OF THE TIME OF CONTACT BETWEEN THE TESTSPECIMEN AND THE HOTTEST PART OF THE BUNSENBURNER FLAME BEFORE A BURNING FOR FIVE SECONDS TAKES PLACE

( CONTINUED )

TEST FLUID USED: THE BENZYLALCOHOL MODIFICATION OF THE SAME TETRA ISOPROPYLTITANATE/ZINCOCTOATE PRODUCT (WITH $TiCl_4$ CATALYST).

| AT A TEMPERATURE OF THE FLUID (OBTAINED BEFORE FLAME TEST) IN °C. | IN °F. | TIME REQUIRED TO OBTAIN A 5 SECOND BURNING TIME (IN sec) |
|---|---|---|
| 130°C. | 266°F. | 39 |
| 165 | 329 | 26 |
| 180 | 356 | 20 |
| 225 | 436 | 12 |
| 250 | 482 | 6 |
| 275 | 526 | 3 |
| 300 | 572 | 0 |

THE RESULTS ARE PLOTTED IN FIGURE 1.

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TABLE 104.

COMPARATIVE TESTS OF THE INFLAMMABILITY OF VARIOUS MATERIALS IN CONTACT WITH AN OPEN BUNSENFLAME ( HOTTEST PART) WHEN STARTED WITH THE MATERIAL AT ROOM TEMPERATURE :

| | |
|---|---|
| DIMETHYL DIETHOXYSILANE ..... | BURNS IMMEDIATELY AND MAINTAINS THE FLAME. |
| DIDODECYL-DIPHENYL SILANE .. ( DOW QF 6-7009) | FLASHES IN 60 seconds. BURNS CONTINUOUSLY AFTER 90 seconds. |
| SILICONE FLUID 510-50 .... (DOW) | FLASHES AFTER 120 seconds AND DECOMPOSES WITH FORMATION OF A WHITE SKIN. |
| SAME INHIBITED ..... | SHOWS HIGHER RESISTANCE THAN UNINHIBITED. |
| TETRA 2 ETHYL HEXYL TITANATE (DUPONT TETRAKIS TITANATE) | BURNS AFTER 2 SECONDS. |
| TRIS DICHLORO PROPYL PHOSPHATE: | FLASHES AFTER 90 seconds, TURNS BLACK WITHOUT SUPPORTING A FLAME. |
| TRI-2 ETHYL HEXYL PHOSPHATE COMMERCIAL FLEXOL (Union Carbide) | FLASHES STRONGLY AFTER 60 seconds MAINTAINS FLAME FOR 5 SECONDS AFTER 100 sec BUT GOES OUT ULTIMATELY AFTERWARDS. |
| NATURAL HIVACUUM TYPE PUMPOIL | FLASHES AFTER 80 seconds AND CONTINUOUSLY BURNS AFTER 100 seconds. |

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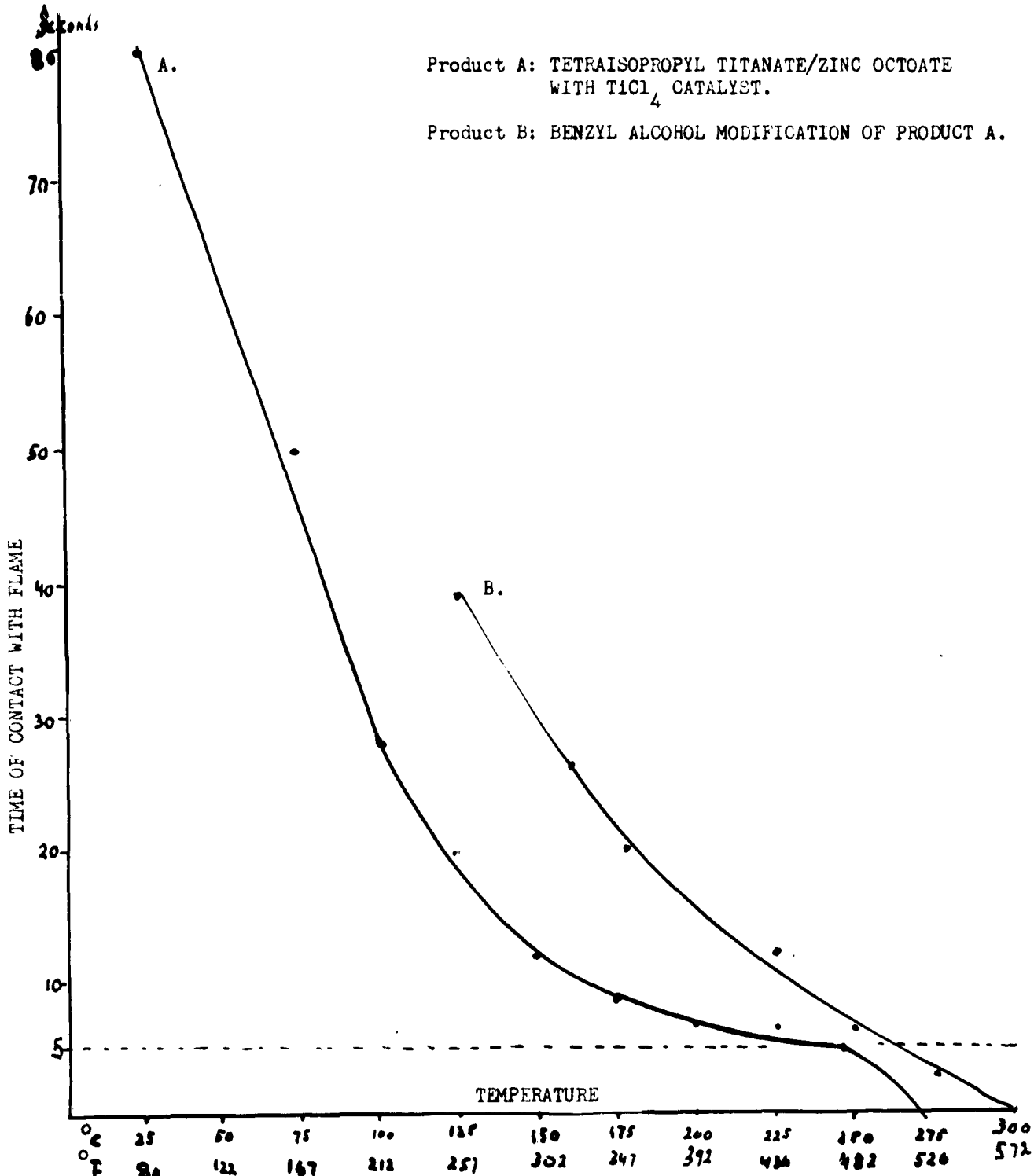


FIGURE 1. TIME OF CONTACT OF TEST FLUIDS WITH BUNSENBURNER FLAME, HELD AT AN ANGLE OF 60 DEGREES FROM THE HORIZONTAL vs TEMPERATURE OF THE FLUIDS BEFORE REACHING A 5-SECOND BURNING TIME.

## SECTION B. RESUMING THE STUDY OF THE EFFECT OF TITANIUM TETRA CHLORIDE AS CATALYST IN THE PREPARATION OF THE EXPERIMENTAL PRODUCT FROM TETRA ISOPROPYL TITANATE AND BASIC ZINC OCTOATE.

### INTRODUCTION

TABLES 105 - 119 give various preparations of the reaction product using 1 part tetraisopropyl titanate and 3 parts zinc octoate with small amounts of titanium tetrachloride. This amount is varied slightly between tests, but it appeared that an increase in titanium tetra chloride does not increase the effect of the reaction. The product obtained from this reaction stands up more successfully in the oxidation-reduction tests than the corresponding product produced with aluminum chloride as catalyst; but it is further being improved and is more uniform in its characteristics when it is further reacted and vacuum distilled with benzyl alcohol. Generally 1 part benzyl alcohol and 2 parts of the reaction product gives the most stable material. FIGURE 1 in SECTION A of this report has shown already an example of the stabilizing influence of this benzyl alcohol modification.

The reaction between the titanate and the zinc octoate are further influenced by the control of the vacuum reaction when a capillary tube is inserted into the vacuum distillation and is used to control the uniformity of the boiling under vacuum.

The repeated preparations were made with careful consideration of an as-far-as-possible removal of low cut materials which might influence the flame- and the self-extinguishing-property tests. They were prepared also as starting materials for new developments introducing into these complexes additional groups, such as phosphorus-, or chlorine,-containing groups in efforts to study their influence on the fire exposure tests.

Another problem which came up in the work on this Section B was that the company which produced the basic zinc octoate (Nuodex Products) tried to change the supplying of the material with 22% zinc to a material with 18% zinc. This was later abandoned, and the original material was supplied again; but TABLES 118-119 showed that this announced change was of no influence on the reaction. It was found that this change in zinc

(Continued on page 30.)

TABLE 105.

RESUMED STUDY OF THE REACTION BETWEEN 1 part ( by weight) TETRAISOPROPYLTITANATE (120 g.)

AND 3 parts " " BASIC ZINC OCTOATE ( 360 g.)

IN PRESENCE OF 2-3 DROPS TITANIUM TETRA CHLORIDE CATALYST

( T 42- 76)

HEAT DEVELOPED UPON MIXING.

| TIME min. | TEMPERATURE C. | VARIAC # | PRESSURE mm. | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|
| - | 24 (75°F.) | 50 | 2 -10 | - | BUBBLING GENTLY |
| 35 | 30 | 60 | | | FEW DROPS DISTILLATE |
| 60 | 95 | 60 | | 20 | CLEAR YELLOW LIQUID |
| 85 | 100 (212°F.) | 60 | | 40 | |
| 90 | 105 | 60 | | 60 | |
| 100 | 115 | 60 | | 85 | |
| 110 | 115 | 60 | | 110 | |
| 120 | 105 | 60 | | 135 | |
| | | | | | C U T I |
| 165 | 170 (338°F.) | 60 | | 10 | DARK LOW VISCOUS MATERIAL |
| 215 | 183 (361°F.) | 60 | | 20 | |
| | | | | | C U T II |
| 280 | PRODUCT CAME OVER BETWEEN 305 °AND 315°C. | | | | |
| | | | ..... | 275 ml. | |
| | | | | | C U T III |

THE TEMPERATURE DROPPED. THERE STILL WAS A LOW VISCOUS MATERIAL IN THE FLASK. ( T 42- 76-2)

BENZENE WAS ADDED AND THE DISTILLATION RESUMED AS T 42- 77

T 42-77 : DISTILLATION OF THE FLASK RESIDUE WITH ADDED BENZENE.

| | | | | | |
|---|---|---|---|---|---|
| - | 25 (77°F.) | 40 | ATM. | - | BENZENE BEGINS TO COME OVER |
| 30 | 80 (176°F.) | 50 | | 10 | |
| 45 | 80 | 50 | | 40 | |
| 60 | 80 | 50 | | 80 | |
| | | VACUUM APPLIED | | | |
| 75 | 70 (158°F.) | 40 | 2 - 1 0 | 120 | |
| | | | | | CUT I |
| 90 | 120 (248°F.) | 55 | | 10 | A YELLOW MATERIAL |
| 120 | 125 (257°F.) | 75 | | 15 | |
| | | | | | CUT II |

THE STILL REMAINING FLASK CONTENT HAD A FLASH POINT OF 295°C. (563°F) AND A FLAME POINT OF 319°C. (606°F)

TABLE 106.

(CONTINUATION OF TABLE 105.)

BENZYLALCOHOL MODIFICATION OF THE REACTION PRODUCT OBTAINED AS DISTILLATE ( T 42-76) FROM 1 part TETRA ISOPROPYL TITANATE WITH 3 parts BASIC ZINC OCTOATE IN PRESENCE OF 2-3 drops TITANIUM TETRA CHLORIDE AS CATALYST:

TEST: T 42-80 : USED 153.7 g. DISTILLATE OF T 42-76 AND 100 g. BENZYLALCOHOL.

| TIME min. | TEMPERATURE C. | VARIAC # | PRESSURE mm. | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|
| - | 25 (77°F.) | 40 | 2-10 | - | |
| 25 | 93 (199°F) | 45 | | 3 | CLEAR, COLORLESS LIQUID |
| 35 | 90 | 43 | | 40 | |
| 45 | 88 | 45 | | 50 | |
| 55 | 88 | 45 | | 60 | |
| 65 | 88 | 45 | | 75 | |
| 75 | 90 | 45 | | 90 | |
| 85 | 90 | 55 | | 95 | |
| 110 | 94(201°F.) | 65 | | 100 | |
| | | | | | C U T I ( 80 g.) |
| 125 | 110(230°F.) | 65 | | 5 | CLEAR, SLIGHTLY YELLOW FLUID |
| 140 | 170(338°F.) | 65 | | 10 | WHITE FUMES |
| 160 | 180 | 70 | | 15 | |
| 170 | 180(356°F.) | 70 | | 20 | |
| 180 | 210 | 70 | | 30 | |
| 190 | 230 | 70 | | 40 | |
| 220 | 160 | 75 | | 43 | |
| 230 | 200(392°F.) | 75 | | 43 | FLASK CONTENT TURNED WHITE |
| | | | | | C U T II ( 29 g.) |
| 245 | 290 | 75 | | 10 | |
| 265 | 300/305 (572°F./581°F.) | 75 | | PRODUCT: 120 g. | |

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TABLE 107.

FURTHER STUDIES ON THE TITANIUM TETRA CHLORIDE CATALYST APPLICATION IN THE PREPARATION OF THE REACTION PRODUCT BETWEEN TETRA ISOPROPYL TITANATE AND BASIC ZINC OCTOATE

I. BENZYLALCOHOL MODIFICATION OF THE PREPARATION T 33-92 T 28 - 147

USED 185 g. PRODUCT, THAT IS CUT 4 OF T 33-92

AND 93 g. BENZYLALCOHOL

| TIME min. | TEMPERATURE C. | VARIAC # | PRESSURE mm. | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|
| - | 25 (77°F.) | 45 | 2-10 | - | |
| 30 | 25 | 45 | | - | |
| 45 | 30 | 45 | | - | |
| 120 | 53 | 35 | | - | |
| 145 | 90 | 55 | | - | |
| 170 | 90 (194°F.) | 55 | | 50 | CLEAR CUT |
| 190 | 92 | 55 | | 75 | |
| 210 | 100 | 55 | | 90 | |
| 230 | 147 (296°F.) | 65 | | 100 | STILL CLEAR |
| | | | | | C U T I |
| 260 | 150 | 70 | | 15 | DARK YELLOW |
| 280 | 105 | 70 | | 25 | |
| | | | | | C U T II |
| 315 | 325 (616°F.) | 85 | | 50 | VERY DARK ORANGE, VISCOUS |
| | 327 (620°F.) | | | 125 | |

TOTAL YIELD ..... 141 g.

II. NEW PREPARATION OF THE PRODUCT FROM 1 part by weight ..190 g. TETRA ISOPROPYL TITANATE
3 parts by weight.. 570 g. ZINC OCTOATE
WITH 2 - 3 DROPS Ti $Cl_4$

T 28 - 148

| | | | | | |
|---|---|---|---|---|---|
| - | 30 (86°F.) | 50 | 2 -10 | - | |
| 60 | 92 | 50 | | 10 ml. | CUT I |
| 70 | 112 (233°F.) | 60 | | 60 | |
| 85 | 126 | 60 | | 150 | CLEAR YELLOW LIQUID |
| 90 | 130 | 60 | | 195 | |
| 120 | 100 | 65 | | 225ml | C U T II ( 200 g) |
| 165 | 200 | 65 | | 4 | CLEAR ORANGE CUT III |
| 170 | 315 (598°F.) | 65 | | | PRODUCT COMING OVER |
| 180 | 313 | 65 | | 50 -60 g. | TAKEN AS CUT IV |
| 190 | 296 | 65 | | 15 | COLOR LIGHTER |
| 225 | 310 | 65 | | 30 | |
| 245 | 315 | 65 | | 65 | CLEAR YELLOW FLUID |
| 310 | 314 | 65 | | 165 | TAKEN AS CUT V |
| 330 | 315 | 65 | | 120 | |
| 355 | 315 | 65 | | 200 | |
| 375 | 316 | 65 | | 220 ml. | TOTAL YIELD 310 g. |

A SMALL AMOUNT OF WHITE RESIDUE LEFT IN POT.

TABLE 108.

ANOTHER APPLICATION OF THE TITANIUM TETRA CHLORIDE CATALYST IN THE REACTION BETWEEN TETRA ISOPROPYL TITANATE AND BASIC ZINC OCTOATE

T 42- 81

USED: 1 part by weight ( 180 g) TETRA ISOPROPYL TITANATE
3 parts by weight ( 540 g) BASIC ZINC OCTOATE
2-3 drops $TiCl_4$

HEAT UPON MIXING DEVELOPED.

| TIME min. | TEMPERATURE C. | VARIAC # | PRESSURE mm. | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|
| - | 27 (80°F.) | 50 | 2-10 | - | BUBBLING |
| 30 | 30 | 50 | | - | |
| 60 | 95 (203°F.) | 50 | | 10 | CLEAR DISTILLATE |
| 85 | 105 | 55 | | 30 | |
| 100 | 110 | 55 | | 70 | |
| 110 | 125 (257°F.) | 55 | | 125 | |
| 125 | 125 | 55 | | 175 | WHITE FUMES |
| 140 | 110 | 55 | | 200 | |
| 160 | 100 | 60 | | 215 | |
| 175 | 100 | 65 | | 220 | |
| | | | | | C U T I ( 205 g) |
| 200 | 170 (338°F.) | 70 | | 5 | DARK DISTILLATE, FLASK CONTENT WHITISH YELLOW |
| 220 | 170 | 70 | | 15 | |
| 240 | 185 (365°F.) | 70 | | 35 | |
| 280 | 195 (383°F.) | 70 | | 45 | |
| | | | | | C U T II ( 23 g) |
| 310 | 305 / (581°F.) | | | | |
| | 319 (606°F.) | 70 | | PRODUCT : 256 g. | |

BENZYLALCOHOL MODIFICATION OF THIS PRODUCT ( T 42- 83)

USED : 100 g. BENZYLALCOHOL WITH
200 g. PRODUCT OF TEST T 42-81

| | | | | | |
|---|---|---|---|---|---|
| - | 27 (80°F.) | 45 | 2-10 | - | |
| 60 | 105 (221°F.) | 50 | | 15 | CLEAR, SLIGHTLY YELLOW |
| 75 | 105 | | | 20 | |
| 95 | 105 | 55 | | 50 | |
| 120 | 110 | 60 | | 85 | |
| 160 | 105 | 60 | | 120 | |
| 170 | 105 | 70 | | 130 | |
| | | | | | C U T I |
| 200 | 155 (311°F.) | 70 | | 10 | |
| 210 | 170 (338°F.) | 70 | | 25 | |
| 220 | 180 (356°F.) | 70 | | 40 | |
| 240 | 215 (419°F.) | 70 | | 60 | |
| 260 | 230 (446°F.) | 70 | | 70 | |
| | | | | | C U T II |
| 300 | 300 (572°F.) | 75 | | | |
| | 310 / 320 | 75 | | PRODUCT: 135 g. | |
| | (590°F./608°F.) | - - - - | | | |

TABLE 109.

ANOTHER STUDY OF THE EFFECT OF TITANIUM TETRACHLORIDE AS CATALYST IN THE REACTION BETWEEN TETRA ISOPROPYL TITANATE AND BASIC ZINC OCTOATE ( T 42 - 85)

USED 1 part by weight ( 190 g.) TETRA ISOPROPYL TITANATE

3 parts by weight( 570 g.) BASIC ZINC OCTOATE

2-3 drops TITANIUM TETRA CHLORIDE .

MUCH HEAT DEVELOPED UPON MIXING .

| TIME min. | TEMPERATURE C. | VARIAC # | PRESSURE mm. | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|
| - | 27 (80°F.) | 50 | 2-10 | - | BUBBLING |
| 30 | 50 | 50 | 2-10 | 20 | CLEAR AND COLORLESS |
| 60 | 60 (140°F.) | 60 | | 40 | |
| | | | | | C U T I ( 22 g.) |
| 95 | 95 (203°F.) | 60 | 2-10 | 50 | |
| 120 | 100 | 60 | | 100 | |
| 160 | 120 (248°F.) | 60 | | 130 | |
| 200 | 115 | 60 | | 160 | |
| 220 | 110 | 60 | | 190 | WHITE FUMES |
| 240 | 90 | 60 | | 200 | |
| 260 | 60 | 60 | | 205 | |
| | | | | | C U T II ( 188.8 g.) |
| 280 | 165 (329°F.) | 70 | 2-10 | 10 | YELLOW DISTILLATE |
| 300 | 175 (347°F.) | 70 | | 25 | |
| 320 | 195 (383°F.) | 70 | | 65 | |
| | | | | | C U T III |
| 350 | 305 / 315 (581°F./598°F.) | 70 | | | FLASK CONTENT DID N O T TURN WHITE |
| | | | PRODUCT OBTAINED: | 475.5 g. | |

B E N Z Y L A L C O H O L MODIFICATION T 42-89

USED: 190 g. ABOVE PRODUCT T 42-85 WITH 75 g. BENZYLALCOHOL

| | | | | | |
|---|---|---|---|---|---|
| - | 27 (80°F.) | 50 | 2-10 | - | BUBBLING QUIETLY |
| 30 | 30 (86°F.) | 55 | | - | |
| 45 | 95 | 55 | | 10 | CLEAR AND COLORLESS |
| 70 | 100 | 55 | | 45 | |
| 90 | 98 | 60 | | 55 | C U T I ( 65 g.) |
| 110 | 160 (320°F.) | 60 | | 10 | YELLOW DISTILLATE |
| 120 | 170 | 70 | | 15 | C U T II ( 20 g.) |
| 180 | 230 (446°F.) | 75 | | - | |
| 220 | 303 / 310 (577°F./590°F.) | | ABOUT 175 / 200 ml. PRODUCT CAME OVER . | | |

- - - - - -

TABLE 110.

THE TITANIUM TETRA CHLORIDE CATALYST EFFECT ON THE TETRA ISOPROPYL TITANATE/ZINC OCTOATE REACTION (CONTINUED).

I. T 42-97 USED 190 g. TETRA ISOPROPYL TITANATE WITH 570 g. ZINC OCTOATE AND WITH 2-3 DROPS $TiCl_4$

HEAT UPON MIXING.

| TIME min. | TEMPERATURE C. | VARIAC # | PRESSURE mm. | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|
| - | 27 (80°F.) | 50 | 2 - 10 | - | |
| 30 | 32 (89°F.) | 50 | | 4 | CLEAR COLORLESS DISTILLATE |
| 60 | 95 | 65 | | 10 | SLIGHTLY YELLOW DISTILLATE |
| 70 | 105 (221°F.) | 55 | | 20 | |
| 75 | 110 | | | 30 | |
| 80 | 120 (248°F.) | | | 40 | |
| 85 | 120 | | | 65 | |
| 100 | 120 | | | 115 | |
| 120 | 130 (266°F.) | | | 155 | |
| 140 | 130 | | | 180 | |
| 150 | 130 | | | 210 | WHITE FUMES |
| 170 | 95 | | | 240 | |
| 190 | 80 | 50 | | 245 | |
| 220 | 75 | 65 | | 250 | |
| | | | | | C U T I |
| 280 | 170 (338°F.) | 70 | | 20 | A DARKER YELLOW MATERIAL |
| | | | | | C U T II |
| 320 | 270 (518°F.) | 70 | | - | |
| 360 | 305 / 315 (581°F./598°F.) | | PRODUCT COMING OVER. | | |

II. T 42-98 REPEAT PREPARATION WITH THE SAME AMOUNTS

| | | | | | |
|---|---|---|---|---|---|
| - | 25 (77°F.) | 50 | 2-10 | - | |
| 30 | 32 | 55 | | 10 | CUT I CLEAR AND COLORLESS |
| 60 | 50 | 60 | | - | |
| 90 | 100 | 65 | | 20 | SLIGHTLY YELLOW |
| 100 | 110 (230°F.) | 65 | | 40 | |
| 120 | 110 | 70 | | 65 | |
| 140 | 110 | | | 80 | |
| 160 | 125 (257°F.) | | | 105 | |
| 180 | 130 (266°F.) | | | 135 | |
| 200 | 132 | | | 165 | |
| 220 | 130 | | | 185 | |
| 260 | 130 | | | 210 | |
| 270 | 105 | | | 220 | CUT II ( 190 g) |
| 300 | 175 (347°F.) | 70 | | 10 | DARKER YELLOW MATERIAL |
| 320 | 220 (428°F.) | | | - | |
| 360 | 295 (563°F.) | | | - | |
| 370 | 305/ 315 (581°F./598°F.) | 70 | PRODUCT COMING OVER YIELD 350 g. | | |

- - - -

TABLE III.

MORE PREPARATIONS OF THE TETRA ISOPROPYL TITANATE/BASIC ZINC OCTOATE PRODUCT

WITH T I T A N I U M TETRA CHLORIDE CATALYST

I. T 42-95 USING 190 g. TETRA ISOPROPYL TITANATE AND
570 g. ZINC OCTOATE WITH 2 - 3 DROPS $TiCl_4$ AS CATALYST

M U C H H E A T UPON MIXING.

| TIME min. | TEMPERATURE C. | VARIAC # | PRESSURE mm. | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|
| - | 25 (77°F.) | 50 | 2 - 1 0 | - | BUBBLING SLIGHTLY |
| 30 | 35 | | | - | |
| 60 | 65 (149°F.) | | | 38 ml | C U T I ( 21g) |
| 90 | 100 | 55 | | 45 | |
| 120 | 120 (248°F.) | | | 80 | |
| 140 | 135 | 60 | | 140 | |
| 160 | 140 (284°F.) | | | 180 | |
| 200 | 120 | | | 210 | |
| 240 | 95 | | | 220 | WHITE FUMES |
| 270 | 90 | | | 225 | C U T II ( 190 g) |
| 280 | 165 (329°F.) | 70 | | 15 | YELLOW DISTILLATE |
| 300 | 300 (572°F.) | | | 35 | |
| | BETWEEN 305 AND (581°F.) 315°C. (598°F.) | | | ABOUT 350 g. DISTILLATION PRODUCT | |

II T 42-96
MODIFICATION OF THE PRODUCT OF I WITH BENZYLALCOHOL
USING
120 g. DISTILLATE OF I
55 g. BENZYLALCOHOL

| | | | | | |
|---|---|---|---|---|---|
| - | 25 (77°F.) | 45 | 2 - 1 0 | - | BUBBLING SLIGHTLY |
| 30 | 115 | | | 5 | CLEAR SLIGHTLY YELLOW FLUID |
| 45 | 115 | | | 25 | |
| 60 | 100 | | | 35 | |
| 100 | 125 (257°F.) | 50 | | 45 | |
| 150 | 100 | 60 | | 55 | C U T I |
| 200 | 120 | 70 | | - | |
| 240 | 150 | | | - | WHITE FUMES |
| 260 | 165 (329°F.) | | | 5 | DARKER YELLOW MATERIAL |
| 300 | 185 (365°F.) | | | 15 | C U T II |
| 320 | 305 - 315°C. (581°F. - 598°F.) | | | YIELD : 90 g. MODIFIED PRODUCT. | |

- - - - -

TABLE 112.

CONTINUED STUDIES ON THE $TiCl_4$ CATALYST IN THE TPT/ZINCOCTOATE PRODUCT

I. T 42-99 BENZYLALCOHOL MODIFICATION OF T 42-98
USING 250 g. PRODUCT T 42-98 WITH
120 g. BENZYLALCOHOL

| TIME min. | TEMPERATURE C. | VARIAC # | PRESSURE mm | VOLUME ml | REMARKS |
|---|---|---|---|---|---|
| - | 28 (82°F.) | 50 | 2- 10 | - | |
| 30 | 95 | 55 | | 30 | CLEAR YELLOW DISTILLATE |
| 45 | 93 | | | 55 | |
| 60 | 90 | | | 80 | |
| 100 | 85 | | | 95 | |
| 120 | 130 (266°F.) | | | 100 | |
| 140 | 160 | | | 110 | DARKER YELLOW |
| 180 | 160 (320°F.) | | | 120 | |
| 210 | 160 | 55 | | 125 | C U T I |
| 260 | 230 (446°F.) | 65 | | - | |
| 300 | 305 | | | | PRODUCT COMING OVER |
| | 305/320 (581°F/608°F.) | | | | YIELD ABOUT 200 ml. |

II. T 42-101 USED 190 g. TETRA ISOPROPYL TITANATE SLIGHTLY INCREASED AMOUNT
570 g. ZINC OCTOATE AND 2 ml. $TiCl_4$ OF $TiCl_4$

| | | | | | |
|---|---|---|---|---|---|
| - | 25 (77°F.) | 50 | 2 - 10 | - | |
| 20 | 40 | | | 2 | CLEAR COLORLESS DISTILLATE |
| 60 | 30 | 55 | | 5 | C U T I |
| 65 | 95 | | | 10 | CLEAR, SLIGHTLY YELLOW |
| 75 | 105 (221°F.) | 60 | | 30 | |
| 85 | 105 | | | 50 | |
| 100 | 110 | | | 70 | |
| 110 | 100 | | | 90 | |
| 130 | 100 | 55 | | 110 | |
| 140 | 110 | 60 | | 130 | |
| 150 | 120 | | | 150 | |
| 160 | 125 | | | 170 | DARKER YELLOW |
| 170 | 130 | | | 190 | C U T II |
| 180 | 115 | | | 110 | |
| 190 | 100 | | | 120 | |
| 210 | 80 | | | | |
| 220 | 80 | | | 130 | C U T III |
| 260 | 180 (356°F.) | 70 | | 60 | DARKER YELLOW MATERIAL |
| 300 | 250 | | | - | C U T IV |
| 330 | 305/315 (581°F./598°F.) | | | | PRODUCT COMING OVER YIELD 475 g. |

III. T 42-102 BENZYLALCOHOL MODIFICATION : 175 g. PRODUCT OF II
91 BENZYLALCOHOL

| | | | | | |
|---|---|---|---|---|---|
| - | 25 (77°F.) | 45 | 2 - 10 | - | |
| 70 | 115 | 50 | | 35 | |
| 120 | 95 | | | 90 | |
| 200 | 173 | 60 | | 110 | |
| 280 | 190 | 65 | | 125 | DARKER AND MORE VISCOUS |
| | | | | 170 | CUT I |
| 320 | 310 | 70 | | 25 | GOLDEN YELLOW CLEAR PRODUCT |
| | | | | 50 | |
| 370 | 310 (590°F) | 70 | | 75 ml. | TOTAL MORE VISCOUS THAN WHEN MADE WITH LESS $TiCl_4$ |

 FLASH POINT: 285°C. ( 545°F) FLAME POINT: 300°C. ( 572°F)

TABLE 113.

STUDY OF THE REACTION BETWEEN

190 g. TETRA ISOPROPYL TITANATE

570 g. BASIC ZINC OCTOATE 22 % Zn

WITH 3-4 DROPS $TiCl_4$.

HEAT EVOLVED ON MIXING.

I. T 43-2 PREPARED IN REGULAR SET UP:

| TIME min. | TEMPERATURE C. | VARIAC # | PRESSURE mm. | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|
| - | 80 (176°F.) | 50 | 2 - 7 | - | |
| 45 | 93 | | | 25 | CLEAR COLORLESS FLUID |
| 55 | 100 | | | 50 | CLEAR YELLOW |
| 63 | 100 | | | 75 | |
| 75 | 110 (230°F.) | | | 115 | |
| 90 | 120 | | | 175 | |
| 125 | 70 | | | 235 | C U T I |
| 165 | 78 | 60 | | - | |
| 185 | 120 | | | - | |
| 210 | 240 | | | - | |
| 235 | 280 (536°F.) | | | - | |
| 240 | 312 | 65 | | - | |
| 255 | 320 (608°F.) | 70 | | 100 | LIGHT YELLOW PRODUCT COMING |
| 270 | 323 (612°F) | 70 | | 310 ml. | CLEAR LIGHT YELLOW PRODUCT |

PRODUCT USED FOR MODIFICATIONS

II. T 43 - 5 PREPARED WITH CAPILLARY INTRODUCED INTO THE SET UP

SAME AMOUNTS USED

| | | | | | |
|---|---|---|---|---|---|
| - | 50 (122°F.) | 40 | 2-10 | - | |
| 30 | 50 | 45 | | - | |
| | 95 | | | 10 | |
| | 95 | | | 20 | LIGHT YELLOW CLEAR DISTILLATE |
| | 100 | | | 40 | |
| | 95 | | | 55 | |
| 105 | 95 | | | 80 | |
| 120 | 100 | 55 | | 105 | |
| 130 | 110 | | | 155 | |
| 150 | 110 | | | 230 | C U T I |
| | | | | | IN COMPARISON TO ABOVE TEST ABOUT THE SAME AMOUNT OF CUT I OBTAINED |
| 210 | 180 (356°F.) | 65 | | - | |
| 255 | 312 (593°F) | 70 | | | PRODUCT COMING OVER. |

YIELD ABOUT 400 ml. (ABOVE IT WAS 310 ml),

BEFORE A DECOMPOSITION IN THE FLASK RESIDUE

IS TO BE SEEN

- - - -

TABLE 114.

BENZYLALCOHOL MODIFICATION OF THE REACTION PRODUCT T 43-2

FROM TPT/ ZINCOCTOATE ( WITH $TiCl_4$ ) TEST T 43-3

USED:

425 g. PRODUCT T 43-2 AND

212 g. BENZYLALCOHOL

NO HEAT EVOLVED ON MIXING.

| TIME min. | TEMPERATURE C. | VARIAC # | PRESSURE mm. | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|
| - | 27 (80°F.) | 40 | 2-10 | - | |
| 15 | 28 | | | - | |
| 60 | 28 | | | - | |
| 70 | 120 (248°F.) | 55 | | | STARTING TO COME OVER |
| 85 | 125 | | | 35 | |
| 100 | 125 | | | 95 | |
| 115 | 130 (266°F.) | | | 145 | |
| 125 | 130 | | | 170 | |
| 140 | 140 (284°F.) | | | 190 | |
| 165 | 115 | | | 200 | |
| 180 | 152 (305°F.) | | | 205 | |
| | | | | | C U T I ( 200 g) |
| 220 | 107 (224°F.) | 60 | 2-10 | 15 | CLEAR YELLOW LIQUID |
| 265 | 84 (183°F) | | | 25 | |
| | | | | | C U T II ( 21 g) |
| 325 | 103 (217°F.) | 60 | | 10 | DARK RED OPAQUE LIQUID |
| | | | | | C U T III |
| 370 | 307 | 65 | 2-10 | 10 | CLEAR YELLOW FLUID |
| 380 | 307 (584°F.) | | | 35 | |
| 425 | 209 (408°F.) | | | 335 ml. | |

PRODUCT : 318 g.

SMALL AMOUNT OF WHITE MATERIAL LEFT IN FLASK.

- - - - -

TABLE 115.

MORE STUDIES ON THE TETRA ISOPRYL TITANATE/BASIC ZINC OCTOATE PRODUCT PREPARED WITH TITANIUM TETRA CHLORIDE AS CATALYST:

FLASH AND FLAME POINT TESTS ON THE BENZYLALCOHOL MODIFICATION T 42-89 . TEST T 28 - 146

TESTS MADE ON OPEN CUP WITH BURNER PASSING OVER THE HEATED FLUID:

FLASH POINT .... 285°C .... 545 °F.

FLAME POINT .... 320 °C .... 6 0 8 °F.

TESTS MADE ON A 1:1 MIXTURE OF THE SAME PRODUCT WITH INHIBITED SILICONE FLUID 510 acc.TABLE 100 ( II.REPORT)

FLASH POINT ....270 °C .... 518°F.

FLAME POINT .. 300°C .... 572°F.

REPEAT TEST MADE ON ANOTHER BENZYLALCOHOL MODIFICATION ( T 28-146) MADE FROM ANOTHER PRODUCT PREPARATION ( T 33-92 ) TEST T 28-147.

FLASH POINT ... 265 °C .... 508 °F.

FLAME POINT ... 312 °C .... 593 °F.

- - - -

TABLE 116.

HYDROLYTIC STABILITY TEST

OF THE REACTION PRODUCT BETWEEN TETRA ISOPROPYL TITANATE ( 120 g) AND BASIC ZINC OCTOATE ( 360 g.) IN PRESENCE OF TITANIUM TETRA CHLORIDE AS CATALYST

(T 42- 71 )

TEST No. T 42- 74 : USED 7 5 g .TEST FLUID T 42 -71

2 5 g. WATER WITH

COPPER STRIP : WEIGHT .... 1.3395 g .

AFTER 48 HOURS ROTATING AT 200 °F .

NO CHANGE IN APPEARANCE OF THE OIL.

WEIGHT OF COPPER STRIP AFTER TEST ... 1.3389 g .

WEIGHT LOSS : ..... 0.0006 g .

or 0 . 0 4 5 % LOSS

HYDROLYTIC STABILITY TEST

OF THE BENZYL ALCOHOL MODIFICATION OF A REPEAT PREPARATION OF ABOVE MATERIAL.

T 42-89 T 42- 85

TEST : T-28-145 USED 37.5g.T 42-89 MIXED WITH

37.5 g .INHIBITED SILICONE FLUID 510

25 g. DISTILLED WATER

FOR 48 HOURS AT 200 °F. WITH 5 rpm. ROTATION.

AFTERWARDS SOLUTION SOMEWHAT GREENISH IN COLOR

WEIGHT OF COPPER BEFORE TEST .... 1.7090 g .

AFTER TEST .....1.7009 g .

LOSS .....0.0081 g. or 0.474 %

- - - -

TABLE 117.

OXIDATION RESISTANCE TEST OF THE

BENZYLALCOHOL MODIFICATION OF THE TETRA ISOPROPYL TITANATE/ZINC OCTOATE PRODUCT

WITH TITANIUMTETRA CHLORIDE CATALYST:

TEST T 42 - 82

USED : 50 g. T 42-80 PRODUCT OF TABLE 106.

IN VISCOSITY REDUCED BY ADDITION OF

50 g.INHIBITED DOW SILICONE FLUID OF TABLE 100 ( REPORT No.2)

TOTAL WEIGHT OF APPARATUS ..... 296.1 g.

COPPER STRIP ..... 0.4623 g.(BEFORE TEST) 0.4620 g.AFTER TEST (LOSS: 0.065 %)

ALUMINUM STRIP..... .0 7039 g(BEFORE TEST) 0.7041 gAFTER TEST (LOSS : --)

STEEL STRIP ..... 1 5325 g.(BEFORE TEST) 1.5328 g.AFTER TEST ( LOSS: -- )

TEST OPERATED AT 200 °CENTIGRADE ( 392°F) WITH 5 1.AIR / HOUR.

AFTER 24 HOURS DARKER IN COLOR, BUT NO SEDIMENT

AFTER 48 HOURS SAME

AFTER 72 HOURS DARK IN COLOR, BUT STILL FLUID AND NO SEDIMENT:

WEIGHT AFTER 72 HOURS TEST ..... 279.6 g.

LOSS..... 15.5 g.or 15.5 %

VISCOSITY 1100 cps .

POUR POINT OF THE SAME FLUID BEFORE TEST .... - 70 °F.

AFTER 72 HOURS TEST ... - 45 °F.

- - - -

TABLE 118.

STUDY ON THE USE OF A NEW COMMERCIAL ZINC OCTOATE ( 1 8 %) NUODEX Co.

FOR THE COMPLEXING WITH TETRA ISOPROPYL TITANATE ($TiCl_4$ CATALYST )

T 42- 104

USED: 151 g. ZINC OCTOATE 1 8 % Zn

51 g. TETRA ISOPROPYL TITANATE

2-3 drops $Ti\ Cl_4$

HEAT EVOLVED ON MIXING THE TITANATE WITH THE ZINC OCTOATE AND

AGAIN MORE HEAT ON ADDITION OF THE TITANIUM TETRA CHLORIDE .

| TIME min. | TEMPERATURE C. | VARIAC # | PRESSURE mm. | VOLUME ml | REMARKS |
|---|---|---|---|---|---|
| - | 25 (77°F.) | 45 | 2-10 | - | |
| 60 | 85 | 50 | | 2 | CLEAR, COLORLESS |
| 70 | 85 | 50 | | 27 | |
| 90 | 100 | 50 | | 37 | |
| 110 | 110 (230°F) | 55 | | 55 | |
| | | | | | CUT I |
| 120 | 110 | 55 | | 25 | YELLOW CLEAR DISTILLATE |
| 160 | 100 | 60 | | 30 | FLASK CONTAINER TURNS WHITE |
| 200 | 160 (320°F) | 70 | | 35 | |
| 240 | 260 (500°F.) | 75 | | 40 | |
| | | | | | CUT II (TOTAL 83 g.) |
| 280 | 300 (572°F) | 75 | | - | |

PRODUCT CAME OVER AT 303°C (577°F.) ..... ABOUT 75 ml.

APPEARS TO BE THE SAME PRODUCT AS OBTAINED WITH

ZINC OCTOATE 22% Zn .

O X I D A T I O N TEST WITH 1 part OF THIS PRODUCT AND
1 part INHIBITED SILICONE FLUID 510 T 42-107

WEIGHT OF SET-UP BEFORE TEST ..... 256.5 g.

AFTER TEST ..... 253.5 g. LOSS.... 3 g.

OBSERVATIONS:

TEST MADE WITH ONE STRIP EACH OF Cu Al AND STEEL . AIR: 5 LITER/HOUR

TEMPERATURE 200°C ( 392°F)

AFTER 72 HOURS STILL LIQUID. DARK BROWN IN COLOR, BUT STILL A CLEAR LIQUID

WITHOUT ANY SEDIMENTATION.

TABLE 119.

USING THE INDUSTRIAL ZINCOCTOATE WITH 1.8 % ZINC CONTENT

IN REACTION WITH TETRA ISOPROPYL TITANATE

I. T 43-7 USING 300 g ZINC OCTOATE 18%

100 g. TETRA ISOPROPYL TITANATE

3 - 4 DROPS $TiCl_4$

| TIME min. | TEMPERATURE C. | VARIAC I BOTTOM | VARIAC II TOP | VARIAC III CLAISSEN | PRESSURE mm | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|---|---|
| - | 28 (82°F.) | 45 | 30 | 20 | 2-10 | - | |
| 30 | 85 (185°F.) | | | | | 35 | CLEAR, COLOR- |
| 45 | 95 | | | | | 70 | LESS |
| 55 | 105 (221°F.) | | | | | 100 | |
| 65 | 110 | | | | | 125 | |
| | | | | | | | CUT I |
| 90 | 135 (275°F.) | 55 | 35 | 20 | 2-10 | 40 | CLEAR YELLOW |
| 120 | 100 | | | | | - | |
| 180 | 85 | | | | | - | |
| | | | | | | | CUT II |
| 200 | 175 (347°F.) | 65 | 50 | 30 | | - | |
| 240 | 160 (320°F.) | | | | | - | |
| 250 | 301 (573°F.) | 65 | 60 | 50 | | | CLEAR LIGHT YEL- |
| | | | | | | | LOW PRODUCT |
| | 297 / 301 C | | | | | 175 ml. | COMING |
| | (566°F./574°F.) | | | | | | |

FLASH POINT 264 °C. ... 508 °F.

FLAME POINT 316 °C. ... 600 °F.

II. T 43-8 HYDROLYTIC STABILITY TEST OF THIS PRODUCT T 43-7

ACCORDING TO THE TENTATIVE STANDARD METHOD 3457 ( 15 DEC 55)

COPPER SPECIMEN 1.3 cm x 7.1 cm. 1.5325 g.

AFTER TEST ... 1.5281 g. WEIGHT LOSS 0.044 g. ( 0.28%)

USED ... 75 g. PRODUCT AND 25 g. WATER

AT 200°F WITH 5 r p m

FOR 72 hours.

(Continued from page 14.)

content is not a decrease in content of the basic zinc octoate component in the reaction, but is only the decrease of solids content of the delivered material. The difference consists of the presence of some solvent in the preparation of the octoate and after, under vacuum, such small amounts of solvent had been taken off, the materials are still of the same reactivity in the preparation of the titanate complex.

TABLES 115-117 give new flash point and flame point data and new hydrolytic stability and oxidation resistance tests on the materials of this Section B.

## SECTION C. INFLUENCE OF VARYING THE ALKYL GROUPS IN THE TITANATES IN THEIR ZINC OCTOATE REACTION.

### INTRODUCTION

This Section C gives data on tests where the tetra isopropyl titanate has been replaced by a tetra 2 ethyl hexyl titanate ( TABLE 120.). In TABLES 121-123 the tetra isopropyl titanate was transesterified with tetra hydro furfuryl alcohol, and the resulting material was complexed with zinc octoate. This product was lower in viscosity, but it is still under study.

Further studies using tetra norm butyl titanate, tert. sec. butyl titanate, and tetra benzyl titanate are being discussed in Section D.

- - -

TABLE 120.

REACTING TETRA 2 ETHYL HEXYL ( OCTYL ) TITANATE WITH ZINCOCTOATE

USING TITANIUM TETRACHLORIDE AS CATALYST

I.

T 38 - 80

FIRST MIXED: 140 g. TETRA OCTYL TITANATE WITH

190 g. ZINCOCTOATE

THIS CAUSED A VERY VISCOUS WHITE MATERIAL, ALMOST NOT POURING .

ON ADDING A FEW DROPS OF TITANIUM TETRA CHLORIDE TO THIS VISCOUS MATERIAL, NO SPECIAL EFFECT IS OBSERVED, PROBABLY BECAUSE NO ACTUAL MIXTURE TAKES PLACE WHEN THIS IS DISTILLED UNDER VACUUM A VERY STRONG FOAMING TAKES PLACE AT AROUND (338°F) 170°C. ( 2- 10 mm PRESSURE) AND THE MIXTURE TURNS ORANGE BROWN AND VERY VISCOUS EVEN AT THAT TEMPERATURE:

| TIME min. | TEMPERATURE C. | VARIAC | PRESSURE mm. | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|
| - | 26° (78°F.) | 40 | 2-10 | - | |
| 60 | 85 (185°F.) | | | 3 | |
| 120 | 145 (293°F.) | 50 | | 28 | |
| 140 | 155 | 55 | | 53 | |
| 160 | 152 | | | 78 | |
| 170 | 145 | | | 88 | |
| 185 | 160 (320°F.) | 60 | | 108 | |
| 195 | 165 | | | 118 | |
| 205 | 170 (338°F.) | | | 128 | |

A STRONG FOAMING OCCURRED.

TO BE REPEATED IN A BENZENE SOLUTION.

TABLE 120 (Continued)

RESUMING THE REACTION OF TETRA OCTYL TITANATE AND

ZINCOCTOATE WITH TITANIUM TETRACHLORIDE

IN BENZENE SOLUTION

T 38- 82

DISSOLVED .... 290 g. TETRA OCTYL TITANATE AND

380 g. ZINC OCTOATE IN

100 g. BENZENE

ADDED UNDER SHAKING A FEW DROPS OF TITANIUM TETRA CHLORIDE .

THE BENZENE WAS DISTILLED OFF UNDER ATMOSPHERIC PRESSURE

WITH VARIAC AT 40 AND RAISED TO 55 UNTIL

124 ml. LOW CUT HAD BEEN TAKEN OFF BELOW 100°C .

SOLUTION ALLOWED TO COOL, AFTERWARDS DISTILLED UNDER VACUUM:

| TIME min. | TEMPERATURE C. | VARIAC # | PRESSURE mm. | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|
| - | 26 (78°F.) | 40 | 2 -10 | - | |
| 65 | 110 (230°F.) | 50 | | 5 | |
| 100 | 160 | 60 | | 20 | RAPID DISTILLATION |
| 110 | 163 (325°F.) | | | 40 | |
| 116 | 165 | | | 60 | |
| 130 | 170 (338°F.) | | | 125 | DISTILLATE TURNS YELLOW |
| 140 | 163 | | | 165 | |
| 150 | | | | 195 | |
| 170 | | | | 205 | |
| 185 | | | | | |

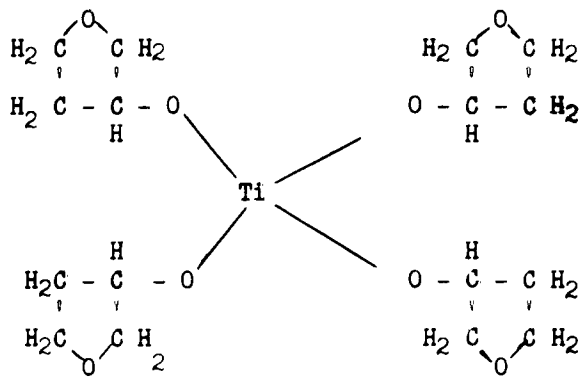
HERE AGAIN OCCURS A SUDDEN VIOLENT FOAMING.

THE REASON IS STILL TO BE FOUND .

- - - -

TABLE 121.

STUDIES USING A TETRA -TETRA HYDRO FURFURYL TITANATE



I. TRANSESTERIFICATION OF 1/2 mole TETRA ISOPROPYL TITANATE WITH ( 142 g.)

T 38- 66 2 moles TETRA HYDRO FURFURYL ALCOHOL ( 176 g)

HEAT DEVELOPED ON MIXING AND A CLEAR REDDISH BROWN COLOR.

| TIME min. | TEMPERATURE C. | VARIAC | VACUUM mm. | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|
| - | 25 (77°F.) | 30 | ATM | - | |
| 50 | 83 (181°F.) | 40 | | 50 | |
| 60 | 86 (187°F.) | 40 | | 75 | |
| 80 | 82 | 45 | | 95 | |
| 100 | 90 (194°F) | 50 | | 105 | ASSUMED TO BE ISOPROPANOL |
| 140 | 100 | 55 | | 115 | |

CUT I .... 103 g.

RESIDUE USED AS T-TETRA HYDROFURFURYL TITANATE
HAS TURNED DARKER IN COLOR AS THE ALCOHOL
IS TAKEN OFF.

II. REPEAT TEST USING 284 g.TETRA ISOPROPYL TITANATE AND

T 38-70

356 g.TETRA TETRA HYDRO FURFURYL ALCOHOL

| | | | | | |
|---|---|---|---|---|---|
| - | 40 (104°F.) | 27 | ATM | - | |
| 50 | 40 | 82 | | 40 | |
| 70 | 50 (122°F) | 90 | | 85 | ASSUMED TO BE ISOPROPANOL |
| 100 | 50 | 84 | | 155 | |
| 130 | 55 | 86 | | 225 | |
| 150 | 55 | 92 | | 280 | |
| 190 | 55 (131°F.) | 102 | | 295 | |

C U T I .... 228 g.

RESIDUE USED AS T-TETRA HYDRO FURFURYL TITANATE.

- - - -

TABLE 122.

STUDIES USING A TETRA -TETRAHYDRO FURFURYL TITANATE

II.

II. T -38-69

REACTING THE TETRA TETRAHYDRO FURFURYL TITANATE OF THE PRECEEDING TABLE WITH BASIC ZINC OCTOATE

USING 60 g TETRA TETRAHYDRO FURFURYL TITANATE

100 g BASIC ZINC OCTOATE IN PRESENCE OF

9 g WATER

| TIME min | TEMPERATURE C | VARIAC | PRESSURE mm | VOLUME ml | REMARKS |
|---|---|---|---|---|---|
| - | 27 (80°F.) | 30 | 2-10 | - | |
| 40 | 75 | 40 | | 10 | ASSUMED TO BE TETRA HYDRO FUR- |
| 50 | 80 | 50 | | 20 | FURYL ALCOHOL |
| 60 | 85 | 55 | | 35 | |
| 65 | 86 | 55 | | 40 | |
| | | | | | C U T I .... 34 g |
| 70 | 105 (221°F.) | 55 | | 5 | YELLOW LIQUID |
| 83 | 110 | 60 | | 10 | |
| 95 | 130 | 60 | | 15 | |
| 100 | 140 (284°F.) | 65 | | 20 | |
| 110 | 180 (356°F.) | 70 | | 30 | |
| | | | | | C U T II |
| 130 | 270 (518°F.) | 70 | | 5 | O R A N G E LOW VISCOUS |
| 135 | 275 (527°F.) | 70 | | 10 | PRODUCT |

MATERIAL WAS COMING, BUT SUDDENLY BUMPED OVER.

TO BE REPEATED IN VIEW OF THE LOW VISCOSITY OF THE HIGH TEMPERATURE CUT

TABLE 123.

STUDIES USING A TETRA - TETRAHYDRO FURFURYL TITANATE

III

III. T 38-77 REPEAT TEST WITH 1/4 MOLE (100 g.) TETRA-TETRAHYDROFURFURYL TITANATE

190 g. ZINC OCTOATE

1/4 MOLE (4.5 g.) WATER.

WHEN WATER IS ADDED, HEAT IS EVOLVED AND THE VISCOSITY DECREASED.

| TIME min. | TEMPERATURE C. | VARIAC | PRESSURE mm. | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|
| - | 26° (78°F.) | 40 | 2-10 | - | |
| 56 | 80 | 50 | | 25 | ASSUMED TO BE TETRAHYDRO |
| 88 | 85 | 50 | | 45 | FURFURYLALCOHOL |
| 120 | 88 (190°F.) | 55 | | 50 ml. | CUT I .... 46 g. |
| 140 | 120 (248°F.) | 60 | | 8 | VERY LIGHT YELLOW LIQUID |
| 163 | 138 | 60 | | 18 | |
| 210 | 155 (311°F.) | 70 | | 33 | LIQUID GETTING DARKER |
| 235 | 145 | 70 | | 53 | CUT II |
| 249 | 270 (518°F.) | 75 | | 5 | DARK BROWN PRODUCT LIKE FLUID |
| 255 | 270 | 75 | | 10 | CUT III |
| 260 | 290 (554°F.) | 75 | | 5 | |
| 265 | 295 | 75 | | 10 | |
| 270 | 296 (564°F.) | 75 | | 15 | |
| 290 | 280 | 75 | | 35 | |
| 302 | 265 (509°F.) | 75 | | 40 | CUT IV PRODUCT: 40 g. |

FLASK RESIDUE SOLIDIFIED.

- - -

## SECTION D. USING A SMALL AMOUNT OF WATER IN THE INTERREACTION BETWEEN TETRA ALKYL TITANATES AND ZINC OCTOATE.

### INTRODUCTION.

This is a continuation of the studies in SECTION C of Report No. 2. In that work it had already been observed that complex products are being obtained in the presence of small amounts of water; but the reaction conditions vary with the alkyl types in the titanates and also with the amounts of water. In view of the fact that the literature, especially the foreign scientific literature, is using water additions in several kinds of metal organic complex formations, it was of interest to pursue this approach further.

### 1. EXPERIMENTS USING DIFFERENT TETRA ALKYL TITANATES AND DIFFERENT AMOUNTS OF WATER.

It is especially interesting to note that not only do different tetra alkyl titanates have different viscosities, their zinc octoate complexes also differ in their viscosity. However, it has not been found that any of these complexes are so much lower in viscosity as to allow their use alone as materials with the desired low pour point ranges of minus 40 to minus 75°F., without the addition of an additional viscosity reducing additive, such as an especially inhibited silicone fluid. TABLE 125 shows a successful preparation of the zinc octoate complex fluid with tetra n butyl titanate and with tetra sec. butyl titanate ( further studied in TABLE 126) and with a new tetra benzyl titanate in TABLE 127. A reaction between tetra 2 ethyl hexyl titanate and basic zinc octoate with a higher amount of water produced, in TABLE 128, a material with a flame point of 604°F.

### 2. EVALUATION TESTS.

What limits the usefulness of the water additive in the reaction is that the resulting product behaves differently under the oxidation-reduction test. It not only shows some formation of a slight sedimentation; it also shows a greater increase in viscosity under the oxidation test together with a higher weight loss in material. The reason for this has not yet been explained. ( TABLES 128-131)

(Continued on page 46.)

TABLE 124.

MORE STUDIES ON THE INFLUENCE OF SMALL AMOUNTS OF WATER ADDITION TO THE TETRA ALKYL TITANATE - BASIC ZINC OCTOATE REACTION I.

I. T 38- 57 USING 142.1 g. TETRA ISOPROPYL TITANATE A L O N E WITH 4.5 g. WATER

THIS WAS AN ATTEMPT TO OBTAIN A TITANATE-DIMER.

ISOPROPANOL WAS DISTILLED OFF AT ATMOSPHERIC PRESSURE, BUT A WHITE PRECIPITATE -PROBABLY PARTIALLY A $TiO_2$ -WAS FORMED INSTEAD OF THE EXPECTED DIMER.

II. USING AS TETRA ALKYL TITANATE A TETRA B U T Y L TITANATE AND ZINCOCTOATE T 38-56

USING 1/4 mole ( 83 5 g) TETRA BUTYL TITANATE ( NORMAL BUTYL TITANATE) 190 g. ZINC OCTOATE AND 1/4 mole ( 4.5 g) WATER

SMALL AMOUNT OF HEAT DEVELOPED ON MIXING. THE MIXTURE REMAINED CLEAR (UNLIKE THE MIXTURE BETWEEN ZINCOCTOATE AND TETRA ISOPROPYL TITANATE). HAD, ON VIGOROUS MIXING WITH THE WATER ADDITION, A CLEAR YELLOW COLOR.

| TIME min. | TEMPERATURE C. | VARIAC # | PRESSURE mm. | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|
| - | 30° (86°F.) | 20 | 2-10 | - | |
| 20 | 50 (122°F.) | 35 | | 20 | CLEAR COLORLESS LIQUID |
| 30 | 45 (113°F.) | 40 | | 30 | PROBABLY BUTYL ALCOHOL |
| 40 | 45 | 45 | | 35 | |
| 50 | 40 | 50 | | 40 | |
| | | | | | C U T I .... 35 g. |
| 80 | 95 (203°F.) | 50 | 2-10 | 20 | VERY LIGHT YELLOW LIQUID |
| 90 | 98 (208°F) | 55 | | 30 | |
| 100 | 95 | 60 | | 35 | |
| 108 | 99 (210°F) | | | 45 | |
| 115 | 100 | | | 55 | |
| 120 | 120 (248°F) | | | 80 | |
| 133 | 140 (464°F.) | | | 85 | |
| 135 | 135 (275°F.) | 65 | | 95 | |
| 140 | 142 (287°F.) | | | 100 | |
| | | | | | C U T II |

FLASK CONTENT SOLIDIFIED BEFORE HIGH TEMPERATURE CUT HAS BEEN OBTAINED.
TO BE REPEATED.

TABLE 125.

MORE STUDIES ON THE INFLUENCE OF SMALL AMOUNTS OF WATER ADDITION

TO THE TETRA ALKYL TITANATE-BASIC ZINC OCTOATE REACTION II

III. T 38-58 REPETITION OF THE TETRA n BUTYL TITANATE / ZINC OCTOATE REACTION

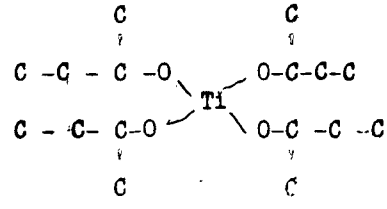
USING THE SAME AMOUNTS OF THE COMPONENTS BUT 1 8 g. WATER (INSTEAD OF 4.5 g.)

| TIME min. | TEMPERATURE C. | VARIAC # | PRESSURE mm. | VOLUME ml. | WEIGHT | REMARKS |
|---|---|---|---|---|---|---|
| - | 30° (86°F.) | 40 | 2-10 | - | | |
| 60 | 50 (122°F.) | | | 100 | | CLEAR COLORLESS, PROBABLY n BUTYLALCOHOL |
| 80 | 50 | | | 105 | | CUT I 66 g. |
| 100 | 75 (167°F.) | 50 | 2-10 | 3 | | CLEAR LIQUID CUT II |
| 130 | 150 (302°F.) | | | 2 | | YELLOW LIQUID CUT III |
| 150 | 295 (563°F.) | | | 20 | | CUT IV |
| 160 | 3 0 0 (572°F.) | 50 | | 20 | | |
| 200 | 3 0 4 (579°F.) | | | 100 ml. | | |

THE PRODUCT ... 86 g.

THIS PRODUCT WAS A VISCOUS MATERIAL, SIMILAR IN APPEARANCE TO THE TETRA ISOPROPYL TITANATE / ZINC OCTOATE DERIVATIVE. THE FLASK RESIDUE WAS SOLID.

IV. T 38- 59 USING TETRA sec BUTYL TITANATE :



USING:

83.5 g. TETRA SEC BUTYL TITANATE
190 g. BASIC ZINC OCTOATE
9 g. WATER

| | | | | | |
|---|---|---|---|---|---|
| - | 40 (104°F.) | 20 | 2-10 | - | CLEAR FLUID, PROBABLY |
| 20 | 44 (111°F.) | 30 | | 30 | sec. BUTANOL |
| 40 | 35 (95°F.) | 40 | | 80 | |
| | | | | | C U T I ( 60 g) |
| 90 | 75 (167°F.) | 50 | | 5 | |
| 120 | 165 (329°F.) | 70 | | 10 | |
| 160 | 285 (545°F.) | 75 | | 20 | |
| | | | | | C U T II |
| 175 | 3 0 5 (581°F.) | 75 | | 10 | |
| 180 | 305 | 80 | | 20 | |
| 190 | 304 (579°F.) | | | 60 | |
| 200 | 302 (575°F.) | | | 60 | |
| | | | | | C U T III ( 66 g) |

VISCOUS YELLOW PRODUCT

- - - -

TABLE 126.

MORE STUDIES ON THE INFLUENCE OF SMALL AMOUNTS OF WATER ADDITION

TO THE TETRA ALKYL TITANATE-BASIC ZINC OCTOATE REACTION III

V. T 38- 63 REPETITION OF THE REACTION WITH TETRA SEC.BUTYL TITANATE, USING L E S S WATER

USED: 100 g. TETRA SEC.BUTYL TITANATE
190 g. ZINC OCTOATE AND
4.5 g .WATER

WHEN TITANATE AND ZINCOCTOATE ARE MIXED THERE IS A SLIGHT HEAT DEVELOPMENT.

ON ADDITION OF WATER THERE IS MORE HEAT DEVELOPMENT.

| TIME min. | TEMPERATURE C. | VARIAC # | VACUUM mm. | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|
| - | 26°(79°F.) | 40 | 2 - 10 | - | |
| 20 | 42 (107°F.) | | | 15 | CLEAR FLUID, PROBABLY SEC. |
| 30 | 40 (104°F.) | | | 45 | BUTANOL |
| 40 | 35 | | | 85 | |
| 50 | 40 | | | 100 | |
| | | | | | C U T I ( 80 g) |
| 70 | 85(185°F) | 40 | 2 -10 | 10 | |
| 75 | 95(203°F) | 50 | | 22 | |
| 85 | 105(221°F) | 50 | | 32 | |
| 90 | 110(230°F) | 55 | | 48 | |
| 98 | 130(266°F) | 55 | | 63 | YELLOW LIQUID |
| 110 | 165(329°F) | 60 | | 68 | |
| 120 | 230(446°F) | 65 | | 73 | |
| 130 | 280(536°F) | 70 | | 78 | |
| 135 | 290(554°F) | 75 | | 83 | |
| | | | | | C U T II |
| 140 | 3 0 0 | 75 | 2 -10 | 5 | |
| 155 | 305(581°F) | 75 | | 25 | |
| 170 | 3 0 8 | 75 | | 45 | |
| 180 | 298(568°F) | 75 | | 50 | |
| | | | | | PRODUCT : 40 g. |

HERE THE TEMPERATURE DROPPED BELOW 240°C AND THE POT MATERIAL BEGAN TO DECOMPOSE.

DATA FROM THE DU PONT LITERATURE: VISCOSITIES OF KNOWN TETRA ALKYL TITANATES:

TETRA ISOPROPYL TITANATE AT 25°C ..... 4.5 cps.

TETRA SEC.BUTYL TITANATE AT 25°C ..... 1.9 cps.

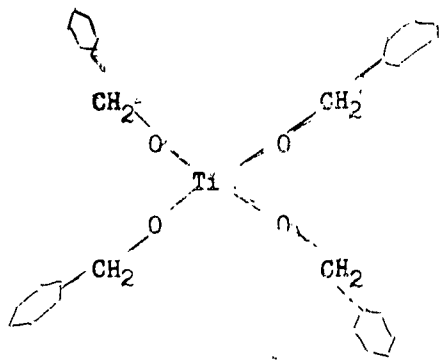
TETRA n-BUTYL TITANATE AT 25°C.....6 7 cps.

TETRA (2 ETHYL HEXYL) TITANATE AT 25°C ..... 1 0 3 cps.

TABLE 127.

MORE STUDIES ON THE INFLUENCE OF SMALL AMOUNTS OF WATER ADDITION TO THE TETRA ALKYL TITANATE-BASIC ZINC OCTOATE REACTION IV.

VI. T 38-61 PREPARATION OF TETRA BENZYL TITANATE



PREPARED FROM 106 g. ( 3/8 mole) TETRA ISOPROPYL TITANATE AND 162 g. ( 12/8 mole) BENZYLALCOHOL ( BP 200°C)

TRANSESTERIFICATION UNDER ATMOSPHERIC PRESSURE

| TIME min. | TEMPERATURE C. | VARIAC # | PRESSURE mm | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|
| - | 26°(79°F) | 45 | ATM | - | |
| 20 | 80 (176°F) | | | 15 | |
| 40 | 82 | | | 45 | ASSUMED TO BE |
| 60 | 84 (183°F) | | | 75 | ISOPROPANOL |
| 65 | 104 (219°F) | | | 85 | |
| 68 | 108 (226°F) | | | 88 ml. | |
| | | | | | DISTILLATE 72 g. |

RESIDUE A YELLOW LIQUID, VISCOSITY SIMILAR AS TETRA 2 ETHYL HEXYL TITANATE, USED IN NEXT TEST.

VII. T 38-62 REACTING 130 g. OF THIS RESIDUE (ASSUMED TO BE MOSTLY TETRA BENZYL TITANATE) WITH 190 g. BASIC ZINC OCTOATE AND 18 g. WATER

ON MIXING WITH WATER MORE HEAT IS DEVELOPED AND AN ODOR OF BENZYLALCOHOL

| | | | | |
|---|---|---|---|---|
| - | 27° | 40 | 2-10 | - |
| 10 | 30 (86°F) | | | 6 ml (4 g.) PROBABLY STILL ISOPROPANOL CUT I |
| 40 | 105 (221°F) | 50 | | 5 |
| 75 | 115 (239°F) | 50 | | 70 ODOR OF BENZYLALCOHOL |
| 105 | 120 (248°F) | 60 | | 100 CLEAR, COLORLESS LIQUID |
| 120 | 126 (258°F) | 60 | | 110 C U T II ( 125 g) |
| 150 | 220 (428°F) | 65 | | - |
| 160 | 270 (518°F) | 75 | | 5 YELLOW SLIGHTLY VISCOUS |
| 170 | 290 (554°F) | 75 | | 20 C U T III |
| 190 | 305 (581°F) | 75 | | 5 |
| 220 | 298 (568°F) | 75 | | 25 YELLOW PRODUCT |
| 220 | 300 (572°F) | 80 | | 45 |
| 240 | 250 (482°F) | 80 | | PRODUCT TOTAL : 50 g. |

TABLE 128.

MORE STUDIES ON THE INFLUENCE OF SMALL AMOUNTS OF WATER ADDITION TO THE TETRA ALKYL TITANATE - BASIC ZINC OCTOATE REACTION V.

VIII.T 38-64

VISCOSITY MEASUREMENTS ON THE REACTION PRODUCTS OF PRECEEDING TESTS:

VISCOSITY AT 2 6°C .

1) PRODUCT OBTAINED FROM TETRA ISOPROPYL TITANATE ...(T 40-48) .... 8 020 cps.
2) SAME PRODUCT ,BUT MODIFIED WITH BENZYLALCOHOL... (T 40-44) .... 2 850 cps.
3) PRODUCT OBTAINED FROM TETRA n BUTYL TITANATE ... (T 38-58) ( No. III OF THIS SERIES) ....24 000 cps.
4) PRODUCT OBTAINED FROM TETRA sec.BUTYL TITANATE . (T 38-59) ( No. V OF THIS SERIES) ....28 000 cps.
5) PRODUCT OBTAINED FROM TETRA 2 ETHYL HEXYL (OCTYL) (T 38-53) TITANATE ( TABLE 88 IN II.REPORT) ....21 000 cps.
6) PRODUCT OBTAINED FROM TETRA BENZYL TITANATE ( T38-62) ( No. VII OF THIS SERIES) .... 3 250 cps.

IX. T 38-65 REPEAT TEST: 510 g. TETRA 2 ETHYL HEXYL ( OCTYL) TITANATE
760 g BASIC ZINC OCTOATE WITH THREE MOLES ( 54 g) WATER

| TIME min. | VARIAC I # | VARIAC II # | TEMPERATURE C. | PRESSURE mm. | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|---|
| - | 40 | 40 | 27 (81°F) | 2- 10 | - | - |
| 40 | 50 | 50 | 75 (167°F) | | 20 | |
| 70 | 50 | 50 | 83 (181°F) | | 110 | ASSUMED TO BE 2 ETHYL |
| 90 | 55 | 55 | 90 (194°F) | | 285 | HEXANOL |
| 120 | 60 | 60 | 92 (197°F) | | 425 | |
| 135 | 60 | 60 | 98 (208°F) | | 520 | |
| | | | | | | C U T I .... 454 grams |
| 140 | 65 | 65 | 120 (248°F) | | 10 | YELLOW LIQUID |
| 160 | 70 | 70 | 150 (302°F) | | 80 | |
| 180 | 75 | 75 | 180 (356°F) | | 140 | C U T II |
| 190 | 75 | 75 | 260 (500°F) | | 10 | |
| 210 | 70 | 60 | 300 (572°F) | | 50 | |
| | | | | | | C U T III |
| 215 | 70 | 60 | 305 (581°F) | | 20 | |
| 220 | 65 | 55 | 3 3 0 (626°F) | | 50 | |
| 230 | 60 | 50 | 3 4 0 (644°F) | | 70 | |
| 235 | 60 | 50 | 3 4 5 (653°F) | | 100 | |
| 250 | 60 | 50 | 325 (617°F) | | 140 | |
| 260 | 60 | 50 | 305 | | 150 | P R O D U C T |

IN FLAME POINT TEST A VERY SMALL AMOUNT OF LOW CUT BURNED UP AT 240°C.( 464°F)

AFTERWARDS THE PRODUCT HAD A FLASH POINT OF 2 8 6°C. ( 546°F). AND A FLAME POINT OF 3 1 8 C. ( 6 0 4 F)

TABLE 129.

ANOTHER REACTION BETWEEN TETRAISOPROPYL TITANATE ..... 290 g.

T 38-79 WITH ZINC OCTOATE 22% ..... 760 g.

IN PRESENCE OF .....t..... 18 g.WATER

| TIME min. | TEMPERATURE C. | VARIAC I # | VARIAC II # | PRESSURE mm. | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|---|
| - | 26 (79°F) | 40 | 20 | 2-10 | - | |
| 80 | 35 (95°F) | 40 | 20 | | 130 ml | ASSUMED:ISOPROPA- |
| | | | | | CUT I .. 98 g. | NOL |
| 100 | 98 (208°F) | 50 | 30 | | 40 | YELLOWISH LIQUID |
| 130 | 110 (230°F) | | | | 130 | |
| 165 | 118 (244°F) | | | | 200 ml. | |
| | | | | | CUT II ... 198 g. | |
| 190 | 180 (356°F) | 60 | 35 | | 1 | |
| 200 | 200 (392°F) | 70 | 40 | | 4 | BROWN LIQUID |
| 210 | 212 | | | | 9 | |
| 220 | 230 (446°F) | | | | 12 | |
| 240 | 240 (464°F) | | | | 17 | |
| 250 | 265 (509°F) | | | | 17 | |
| | | | | | CUT III | |
| 263 | 273 (524°F) | 70 | 40 | | 10 | PRODUCT LIKE, BROWN |
| 280 | 280 (536°F) | | | | 15 | |
| 285 | 295 (563°F) | | | | 25 | MORE VISCOUS |
| 290 | 298 (568°F) | | | | 30 | |
| | | | | | CUT IV | |
| 298 | 315 (599°F) | 70 | 40 | | 10 | |
| 310 | 318 (604°F) | | | | 50 | CLEAR GOLDEN |
| 320 | 320 (608°F) | | | | 90 | YELLOW PRODUCT |
| 330 | 324 (615°F) | | | | 130 | |
| 340 | 318 | 75 | 40 | | 180 | |
| 350 | 312 (593°F) | | | | 220 | |
| 360 | 310 (590°F) | | | | 250 | |
| | | | | | 245 g. | PRODUCT |

POT RESIDUE VERY VISCOUS, BROWNISH WHITE

T 38-79 30 g.OF THIS PRODUCT MIXED WITH
30 g. INHIBITED SILICONE FLUID

72 HOURS OXIDATION TEST:

| | | | | |
|---|---|---|---|---|
| WEIGHT : ALUMINUM | BEFORE TEST | 0.7272 g. | | |
| | AFTER TEST | 0.7275 g. | INCREASE | 0.0003 g. |
| COPPER | BEFORE TEST | 0.4461 g. | | |
| | AFTER TEST | 0.4420 g. | LOSS | 0.0041 g. |
| STEEL | BEFORE TEST | 1.5637 g. | | |
| | AFTER TEST | 1.5639 g. | INCREASE | 0.0002 g. |

SOME SEDIMENT WEIGHT LOSS .... 37 %

TABLE 130.

F O U R  B A L L  W E A R  TEST ON THE TETRAISOPROPYL TITANATE - BASIC ZINC OCTOATE PRODUCT PREPARED IN PRESENCE OF WATER

I. PREPARATION OF THE TEST MATERIAL :

T-40- 72

USED 425 g. ZINC OCTOATE 22% Zn

158 g. TETRA ISOPROPYL TITANATE

23 g. WATER

| TIME min. | TEMPERATURE C. | PRESSURE mm. | VARIAC | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|
| - | 28 (82°F) | 3.5 | - | - | |
| 20 | 29 | 3.5 | 40 | 10 | ISOPROPANOL COMING OVER SLOWLY |
| 60 | 29 (84°F) | 3.5 | 40 | 30 | |
| 90 | 29 | 3.5 | 40 | 80 | |
| 120 | 95 (203°F) | 3.5 | | | C U T I ..... 60 g. |
| 130 | | 4.0 | | | A CLEAR YELLOWISH FLUID APPEARS |

PRODUCT CAME OVER BETWEEN 295 °AND 305 °C.

II. FOUR BALL WEAR TEST :

30 minutes 60 °C. (140 °F.) 20 Kg.

BALL # 1 SCAR .... 2.98

2 " ... 3.20

3 " ... 2.81

9.03 ... 3.03 (average) FACTOR 0.145

4

SCAR ..... 0.439 mm.

- - - -

TABLE 131.

MORE OXIDATION REDUCTION TESTS ON PRODUCTS MADE

WITH WATER ADDITION DURING THE REACTION

I. T 38 -68

PRODUCT MADE WITH TETRA n BUTYL TITANATE / ZINCOCTOATE
83.5 g. 190 g.
IN PRESENCE OF 18 g.WATER
T 38 -58

TEST MADE WITH ONE STRIP EACH OF COPPER
ALUMINUM AND
STEEL

TEST AT 200°C. (392°F.)

AIR FLOW ..... 5 LITER PER HOUR.

AFTER 72 HOURS THERE WAS A MODERATE AMOUNT OF A SEDIMENTATION

FLUID BROWN AND CLOUDY.

II. T 38-68

PRODUCT MADE WITH TETRA ISOPROPYL TITANATE / ZINC OCTOATE
285 g. 760 g.
IN PRSENCE OF 20 g.WATER
T 40-68

TEST MADE WITH ONE STRIP EACH OF COPPER
ALUMINUM AND
STEEL

TEST AT 198°C. (388°F.)

AIR FLOW ..... 5 LITER PER HOUR

AFTER 72 HOURS TEST THE MATERIAL WAS A DARK FLUID, BUT

VERY VISCOUS AFTER COOLING TO R.T.

- - -

( Continued from page 37)

4. EMISSION SPECTROSCOPIC TESTS COMPARING THE PRODUCTS MADE WITH DIFFERENT CATALYSTS.

The work has established earlier that the reaction between tetra isopropyl titanate and zinc octoate produces a better yield of complex matter when a catalyst is being used, such as aluminum chloride; and the emission spectra show on these products a strongly increased intensity of the titanium lines. Then the use of titanium tetrachloride brought an improved oxidation resistance test of the reaction product. Further-on the reaction in the presence of water brought a more complete freeing of the isopropyl groups and therefore a more complete new reaction product.

Now these products have been subjected to comparative emission spectroscope qualitative tests. The report from the spectrochemical laboratory indicates that the product made with titanium tetra chloride and the product made in the presence of water ( T-38-79) have about the same intensity of the titanium lines. The intensity of the titanium line in the product made with aluminum chloride as catalyst (T 40-74) is considerably higher. The zinc line in all three products appears in about the same intensity.

The reason for these observations is still to be explored.

- - -

## SECTION E. THE INTRODUCTION OF PHOSPHORUS GROUPS INTO TITANATE COMPOUNDS. (Continued from Report 2, Section D.)

### INTRODUCTION.

In the preceding Sections the production of material for this project showed differences in their flash point and flame point characteristics primarily in respect to the degree of the complex formation in the product and the elimination of low cuts. The difference between the distillation ranges of the non complexed and the complexed materials is great enough to aim for a quite complete separation of the materials. This difference in distillation range goes parallel to the difference in flame points, and that allows a quite high range for the flame points of these materials.

Another aim of this group , however, is to explore the influence of the introduction of new groups which might act as additional flame retarders, or as factors to increase the self-extinguishing properties, or to obtain ultimately non-burning properties, under such conditions as might prevail in the hydraulic systems of airplanes, missiles or space craft. Groups which are under consideration here are the phosphorus group, the halogens, and the nitrogen groups, and ultimately perhaps, combinations between these groups, in the titanate fluids which are under development here.

This Section E is concerned with the further study of the introduction of phosphorus.

### 1. EXPERIMENTS USING TRI-2-ETHYL HEXYL PHOSPHATE

In TABLES 132-137 a tri octyl phosphate, or tri-2-ethyl hexyl phosphate is being reacted with either tetra isopropyl titanate or with tetra octyl titanate ( tetra 2-ethyl hexyl titanate) using either aluminum chloride or titanium tetrachloride as catalyst. The resulting products have a distillation range, under vacuum, of 203°/225°C. (397°/437°F.) In TABLE 135 where a special capillary was installed into the distillation a cut was obtained at 240°C. (464°F.) and up to 255°C.(491°F.).

These materials are to be studied further as possible viscosity reducing components for the products in order to replace the inhibited silicone fluids as viscosity reducer. The development is still under study.

(Continued on page 52.)

SECTION E-1 USING TRI-2-ETHYL HEXYL PHOSPHATE.

TABLE 132.

RESUMED STUDIES ON THE INTRODUCTION OF PHOSPHATES INTO TITANATE COMPOUNDS

T 42 - 72

REACTING : TRI - 2 ETHYL HEXYL PHOSPHATE or TRI OCTYL PHOSPHATE ( TOF)

WITH TETRA ISOPROPYL TITANATE ( TPT)

IN THE PRESENCE OF ALUMINUM CHLORIDE AS CATALYST

USING : 120 g.TOF WITH 60 g. TPT IN PRESENCE OF 0.5 g. $AlCl_3$

NO HEAT EVOLVED ON MIXING .

| TIME min. | TEMPERATURE C. | VARIAC # | PRESSURE mm. | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|
| - | 25° (77°F) | 45 | 2 - 10 | - | BUBBLING GENTLY |
| 35 | 30 (86°F) | 50 | | - | SAME |
| 60 | 55 (131°F) | 55 | | - | BUBBLING RAPIDLY |
| 85 | 128 (262°F) | 55 | | - | DISTILLATE BEGAN |
| 100 | 140 (284°F) | 60 | | 35 ml. | CLEAR COLORLESS DISTILLATE |
| 135 | 140 | 60 | | 63 ml. | |
| | | | | | C U T I |
| 140 | 110 (230°F) | 60 | | - | TEMPERATURE DROP |
| 155 | 170 (338°F) | 60 | | 3 | DISTILLATE CLEAR, SLIGHTLY YELLOW |
| 165 | 200 (392°F) | 60 | | 23 | |
| 175 | 200 | 60 | | 33 | |
| 180 | 203 (397°F) | 60 | | 53 | |
| 185 | 203 | 60 | | 73 | |
| 190 | 203 | 60 | | 93 | |
| 195 | 203 | 60 | | 103 | |
| 200 | 203 | 60 | | 113 | |
| | | | | | C U T II |

- - - -

TABLE 133.

REACTING TETRA OCTYL TITANATE WITH TRI OCTYL PHOSPHATE WITH ALUMINUM CHLORIDE CATALYST

T 42 - 79 USED : 1 part ( 60 g.) TETRA 2 ETHYL HEXYL TITANATE ( TETRA OCTYL TITANATE)
AND 2 parts ( 120 g.) TRI 2 ETHYL HEXYL ( OCTYL) PHOSPHATE

SMALL AMOUNT OF ALUMINUM CHLORIDE.

NO HEAT DEVELOPED ON MIXING.

| TIME min. | TEMPERATURE °C. C. | VARIAC # | PRESSURE mm. | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|
| - | 27 ° (81°F) | 40 | 2 -10 | - | BUBBLING GENTLY |
| 30 | 30 (86°F) | 50 | | - | |
| 45 | 30 | 60 | | - | |
| 65 | 100 ° | 60 | | 2 | SLIGHTLY YELLOW DISTILLATE |
| 80 | 150 (302°F) | 60 | | 5 | |
| 110 | 110 (230°F) | 60 | | 30 | |
| 120 | 110 | 60 | | 40 | |
| | | | | | CUT I |
| 140 | 150 | 60 | | 10 | A DARKER YELLOW MATERIAL |
| 150 | 190 (374°F) | 60 | | 20 | |
| | | | | | CUT II |
| 155 | 210 (410°F) | 60 | | 10 | SOMEWHAT LIGHTER COLOR |
| 160 | 210 | 60 | | 40 | |
| 170 | 220 (428°F) | 60 | | 60 | |
| | | | | | CUT III |
| 175 | 195 (383°F) | 60 | | 20 | |
| 180 | 210 | 60 | | 80 | |
| 190 | 215 (419°F) | 60 | | 100 | |
| 200 | 210 | 60 | | 120 | |
| 210 | 210 | 60 | | 140 | |
| | | | | | CUT IV. |

CUT III/IV BASED HERE ON REACTING TRI OCTYL PHOSPHATE WITH TETRA OCTYL TITANATE HAVE ABOUT THE SAME DISTILLATION RANGE AS THE PRODUCT T 42-72 OF TABLE 132 WHERE THE REACTION HAD BEEN MADE BETWEEN TRI OCTYL PHOSPHATE AND TETRA ISOPROPYL TITANATE.

TABLE 134.

MORE REACTIONS BETWEEN TETRA 2 ETHYL HEXYL TITANATE ( TETRA OCTYL TITANATE)

AND TRI 2 ETHYL HEXYL PHOSPHATE ( TRI OCTYL PHOSPHATE)

WITH TITANIUM TETRA CHLORIDE AS CATALYST

I. T 42- 91 USED 60 g. TETRA OCTYL TITANATE

120 g. TRI OCTYL PHOSPHATE AND

2 to 3 DROPS OF Ti $Cl_4$

SLIGHT HEAT DEVELOPMENT ON MIXING

| TIME min. | TEMPERATURE C. | VARIAC # | PRESSURE mm. | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|
| - | 25° (77°F) | 45 | 2- 10 | - | SLIGHT BUBBLING |
| 25 | 28 (82°F) | 55 | | - | |
| 60 | 95 (203°F) | | | 2 | CLEAR, SLIGHTLY YELLOW FLUID |
| 80 | 103 (217°F) | | | 5 | |
| 100 | 135 (275°F) | 60 | | 10 | |
| 140 | 138 (280°F) | | | 35 | |
| | | | | | CUT I |
| 160 | 200 (392°F) | 60 | | - | BOILS VERY RAPIDLY |
| 220 | 220 / 225 (428° / 437°F) | 60 | | 150 -180 ml. | LIGHT GREENISH YELLOW DISTILLATE COMING. DIFFICULT TO CONTROL BECAUSE OF SEVERE BUMPING. |

II. T 42-92 REPEATED WITH MORE CATALYST

USED 40 g. TETRA OCTYL TITANATE WITH 80 g. TRIOCTYLPHOSPHATE AND 10 to 15 DROPS Ti $Cl_4$ SLIGHT HEAT FREED

| | | | | | |
|---|---|---|---|---|---|
| - | 25° (77°F) | 45 | 2 -10 | - | |
| 15 | 27 (81°F) | 50 | | - | STILL NOT BUBBLING |
| 45 | 39 (102°F) | | | - | SLIGHT BUBBLING |
| 70 | 80 (176°F) | | | 4 | CLEAR, SLIGHTLY YELLOW FLUID |
| 90 | 93 (199°F) | | | 5 | |
| 110 | 195 (383°F) | 45 | | 10 | CLEAR DISTILLATE |
| 112 | 195 | | | 20 | |
| | | | | | CUT I |
| 120 | 205 (401°F) | 50 | | 10 | CLEAR YELLOW FLUID |
| 140 | 210 (410°F) | | | 30 | |
| 160 | 205 | | | 45 | |
| | 205 - 210 ..... (401° - 410°F.) | | | 80 | YIELD IN CUT II |

TABLE 135.

REACTING TETRA 2 ETHYL HEXYL TITANATE ( TETRA OCTYL TITANATE )

WITH TRI 2 ETHYL HEXYL PHOSPHATE ( TRI OCTYL PHOSPHATE )

IN PRESENCE OF TITANIUM TETRA CHLORIDE AS CATALYST

T-28 - 152

USED: 120 g. TRI OCTYL PHOSPHATE

60 g. TETRA OCTYL TITANATE WITH 3-4 DROPS Ti $Cl_4$

IN THIS DISTILLATION A CAPILLARY WAS USED TO AVOID "BUMPING" AND TO GET A SHARPER FRACTIONATION.

| TIME min. | TEMPERATURE C. | VARIAC # | PRESSURE mm. | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|
| - | 28° (82°F) | 45 | 5 | - | |
| 40 | 32 (90°F) | 45 | 4 | - | |
| 55 | 73 (163°F) | 55 | 4 | - | |
| 75 | 73 | 55 | 5 | - | |
| 90 | 73 | 55 | 5 | 5 | LIGHT YELLOW |
| 105 | 85 (185°F) | 55 | 5 | 5 | |
| 135 | 87 (189°F) | 55 | 5 | 5 | |
| 150 | 86 (187°F) | 55 | 6 | 10 | |
| | | | | | C U T I |
| 165 | 90 (194°F) | 55 | 11 | - | |
| 190 | 120 (248°F) | 60 | 8 | 10 | CLEAR COLORLESS. |
| 210 | 220 (428°F) | 65 | 10 | 10 | |
| | | | | | C U T II |
| | POT CONTENT STILL VERY FLUID, DARK ORANGE | | | | |
| 215 | 235 (455°F) | 65 | 8 - 10 | 25 | ml. DARK ORANGE. BUMPED OVER |
| | | | | | C U T III |
| 220 | 237 - 240° | 65 | 8 -10 | 25 | STRAW COLORED |
| 225 | 240 (464°F) | 70 | 8 | 50 | COMING OVER NICELY |
| 235 | 240 | 70 | 8 | 75 | |
| 240 | 240 | 70 | 8 | 100 | |
| 245 | 240 | 70 | 8 | 125 | |
| | | | | | C U T III |
| 250 | 245 - 255° (473° - 491°F.) | 70 | 8 | 40 | ORANGE COLOR |

TO BE REPEATED AS EVENTUAL DILUENT FOR THE TETRAISOPROPYL TITANATE/ ZINC OCTOATE PRODUCT.

(Continued from page 47.)

In TABLES 136-137 the aluminum or titanate chloride catalysts were replaced by phosphorus pentoxide. The highest cut with aluminum chloride came over at 195°C (383°F), and with phosphorus pentoxide at 200°C ( 392°F.), indicating no essential difference between the effects.

2. USING AN ALIPHATIC AND AN AROMATIC PHOSPHATE ( TABLES 138/139).

In TABLE 138 again a different approach is being used with the aim of introducing the phosphorus into the complex matter between the titanate and zinc octoate. At the same time it was taken into consideration that the organic aliphatic phosphate results with tetra alkyl titanate in fluids of a distillation range under vacuum of around 200°C. (392°F.). The aromatic phosphates, such as tri cresyl phosphate, result with tetra isopropyl titanate in solids. Here one-half aliphatic and one-half aromatic phosphate was reacted, and the resulting product was afterwards reacted with zinc octoate instead of reacting the zinc octoate with tetra alkyl titanate itself. In TABLES 138-139 a reaction product is obtained from a distillation range of above 300°C. ( 572°F.) under vacuum. This product is being studied further.

3. USING DI-2-ETHYL HEXYL PHOSPHORIC ACID. ( TABLES 140-144).

Earlier, organo phosphoric acid was used in reaction with the alkyl titanate, in particular, di-2-ethyl hexyl phosphoric acid (Section D-1, Report 2.). Now the acid was first reacted with the alkyl titanate and the reaction product further reacted in zinc octoate. The resulting product varied with the ratio between the first reaction product and the zinc octoate. TABLE 140 shows that in reacting tetra octyl titanate with di-2-ethyl hexyl phosphoric acid and then reacting one part of the resulting material with 3 parts basic zinc octoate a product is being obtained with a distillation range of 310-320°C. ( 590°-608°F.), under vacuum, which was modified with benzyl alcohol and showed good results in oxidation-reduction tests of TABLE 144.

Phosphorus pentoxide was not successful in these tests. ( TABLE 143.)

- - -

TABLE 136.

MORE ABOUT THE REACTION BETWEEN TETRA ISOPROPYL TITANATE AND TRI OCTYL PHOSPHATE

I. T 42-100 REACTION WITH A L U M I N U M C H L O R I D E AS CATALYST

USED: 60 g. TETRA ISOPROPYL TITANATE
120 g. TRI OCTYL PHOSPHATE AND 0.5 g. $AlCl_3$

| TIME min. | TEMPERATURE C. | VARIAC # | PRESSURE mm. | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|
| - | 25° (77°F) | 45 | 2-10 | - | |
| 30 | 105 (221°F) | 50 | | 5 | CLEAR COLORLESS DISTILLATE |
| 40 | 108 (226°F) | | | 10 | |
| 60 | 115 (239°F) | | | 30 | |
| 70 | 115 | | | 40 | |
| 80 | 115 | | | 55 | |
| 150 | 80 (176°F) | | | 60 | |
| | | | | | CUT I |
| 180 | 120 (248°F) | 55 | | - | |
| 200 | 180 (356°F) | | | 10 | |
| 220 | 180 | 60 | | 20 | |
| 240 | 195 (383°F) | 55 | | 80 | |
| 250 | 195 | | | 120 | |
| | | | | | CUT II |

II. T 42-103 SAME WITH PHOSPHORUS PENTOXIDE AS CATALYST
USED: 60 g. TETRA ISOPROPYL TITANATE
120 g. TRIOCTYL PHOSPHATE AND 0.5 g. $P_2O_5$

| | | | | | |
|---|---|---|---|---|---|
| - | 25 (77°F) | 40 | 2 - 10 | - | |
| 20 | 30 (86°F) | | | - | BOILING RAPIDLY |
| 60 | 120 (248°F) | 45 | | 10 | CLEAR AND COLORLESS |
| 80 | 110 (230°F) | 40 | | 20 | |
| 100 | 100 | 30 | | 30 | COMES VERY RAPIDLY |
| 105 | 95 (203°F) | 30 | | 40 | |
| 200 | 50 (122°F) | 45 | | 45 | |
| 220 | 120 | | | 45 | |
| 240 | 120 | | | 60 ml. | C U T I |
| 380 | 125 (257°F) | 55 | | 120 | CLEAR AND COLORLESS C U T II |

THE 195°C. (383°F) CUT DID HERE NOT APPEAR AS IN I. (WITH $AlCl_3$)

TEST No. II IS TO BE REPEATED ( TABLE 137. )

TABLE 137.

THE USE OF PHOSPHORUS PENTOXIDE IN THE REACTION BETWEEN

TRI OCTYL PHOSPHATE AND

TETRA ISOPROPYL TITANATE

T 42- 108

USED: 60 g. TETRA ISOPROPYL TITANATE

120 g. TRIOCTYL PHOSPHATE

0.5 g. PHOSPHORUS PENTOXIDE

NO HEAT UPON MIXING

| TIME min. | TEMPERATURE C. | VARIAC # | PRESSURE mm. | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|
| - | 25° (77°F) | 40 | 2-10 | - | |
| 30 | 100 | 45 | | - | BOILING GENTLY |
| 60 | 100 | 55 | | 10 | |
| 90 | 110 (230°F) | 50 | | 35 | C U T I |
| 120 | 150 (302°F) | 50 | | 5 | CLEAR DISTILLATE, STRONG FOAMING, INSPITE OF CAPILLARY |
| 130 | 155 (311°F) | 50 | | 10 | |
| 140 | 160 (320°F) | 45 | | 15 | |
| 160 | 200 (392°F) | 40 | | 35 | STRONG FOAMING |
| 180 | 200 | 40 | | 55 | |
| 200 | 190 (374°F) | 40 | | 85 | |
| 200 | 193 (379°F) | 40 | | 100 | |
| 230 | 185 (365°F) | 40 | | 105 | |
| | | | | | C U T II |

FLASH POINT OF DISTILLATE ... 85°C.( 185°F)

TABLE 138

REACTING TETRA ISOPROPYL TITANATE WITH AN ALIPHATIC A N D AN AROMATIC ORGANO-PHOSPHATE

I. T 42- 110 USED 60 g. TETRA ISOPROPYL TITANATE

60 g. TRI CRESYL PHOSPHATE A N D

60 g. TRI OCTYL PHOSPHATE

NO HEAT EVOLVED UPON MIXING

| TIME min. | TEMPERATURE C° | VARIAC # | PRESSURE mm | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|
| - | 30° (86°F) | 40 | 2 - 1 0 | - | |
| 50 | 45 (113°F) | 45 | | | DROP OF CLEAR FLUID |
| 60 | 105 (221°F) | 45 | | 5 | DISTILLATE CLEAR YELLOW |
| 80 | 130 (266°F) | 40 | | 10 | |
| 100 | 140 (284 F) | 40 | | 25 | |
| 110 | 140 | 40 | | 35 | |
| 140 | 130 | 40 | | 50 | |
| 160 | 135 (275°F) | 40 | | 52 | |
| 180 | 130 | 40 | | 62 | |
| 190 | 130 | 40 | | 72 | |
| 200 | 120 (248°F) | 40 | | 5 ml. | OF A DARKER DISTILLATE. |

DISTILLATION DISCONTINUED IN ORDER TO AVOID SOLIDIFICATION.

II. T 42- 111 FURTHER REACTING THE DISTILLATE OF I WITH ZINC OCTOATE

USED 55 2 g. DISTILLATE OF I

55 2 g. ZINC OCTOATE 1 8 %

COLOR CHANGED TO D A R K R E D AND HEAT EVOLVED

| | | | | | |
|---|---|---|---|---|---|
| - | 25°(77°F) | 45 | 2 - 1 0 | - | |
| 45 | 90 (194°F) | 50 | | 2 | DISTILLATE CLEAR, ALMOST COLORLESS |
| 60 | 115 (239°F) | 55 | | 15 | SLIGHTLY YELLOW |
| 90 | 120 (248°F) | | | 25 | |
| 110 | 120 | | | 35 | |
| 120 | 115 | | | 45 | |
| 130 | 110 (230°F) | | | 55 | |
| 135 | 110 | | | 65 | |
| 150 | 125 (257°F) | 65 | | 75 | WHITE FUMES |
| | | | | | C U T I |
| 180 | 185 (365°F) | 65 | | - | |
| 200 | 235 (455°F) | 70 | | 5 | A DARKER DISTILLATE |
| 210 | 260 (500°F) | | | 25 | |
| 220 | 270 (518°F) | | | 25 | |
| | | | | | C U T II |
| 230 | 2 9 5(563°F) | 70 | | 10 | A MATERIAL IS COMING WHICH APPEARS LIKE THE PRODUCT FROM TPT/ZnOCT. |
| 240 | 295 | 70 | | 15 | |
| 260 | 250 (482°F) | 70 | | | TEMPERATURE DROPPING |

( TO BE REPEATED)

TABLE 139.

REPEAT TEST: REACTING TETRA ALKYL TITANATE WITH AN ALIPHATIC A N D AN AROMATIC ORGANOPHOSPHATE

I. T 42- 112 USED: 120 g. TETRA ISOPROPYL TITANATE

120 g. TRI OCTYL PHOSPHATE AND

120 g. TRI CRESYL PHOSPHATE

NO HEAT EVOLVED UPON MIXING.

| TIME min. | TEMPERATURE C. | VARIAC # | PRESSURE mm. | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|
| - | 30 °C (86°F) | 30 | 2 - 1 0 | - | |
| 30 | 70 (158°F) | 35 | | - | |
| 90 | 140 (284°F) | 30 | | 20 | YELLOW DISTILLATE |
| 100 | 140 | 30 | | 45 | |
| 120 | 140 | 30 | | 70 | |
| 140 | 160 (320°F) | 30 | | 110 | |
| 160 | 155 (311°F) | 30 | | 130 | |
| 200 | 150 (302°F) | 30 | | 140 | |
| 210 | 150 | 30 | | 150 | |

II. REACTING 128.8 g. OF THIS DISTILLATE I WITH

128.8 g. ZINC OCTOATE 18% T 42- 113

COLOR CHANGED TO DEEP RED UNDER HEAT DEVELOPMENT

| | | | | | |
|---|---|---|---|---|---|
| - | 27°(81°F) | 40 | 3 mm. | - | |
| 35 | 90 (184°F) | 45 | | 10 | CLEAR DISTILLATE |
| 45 | 95 (203°F) | | | 20 | |
| 60 | 100 | | 2 mm. | 40 | |
| 70 | 100 | | | 55 | |
| 90 | 110 (230°F) | | | 75 | |
| 120 | 115 (239°F) | | | 85 | |
| 140 | 130 (266°F) | | | 95 | DISTILLATE CLEAR, BUT MORE YELLOW |
| 150 | 135 (275°F) | | 3 mm. | 105 | |
| 165 | 140 (284°F) | | 4 mm. | 125 | |
| 180 | 150 (302°F) | 50 | | 140 | |
| 210 | 230 (446°F) | 60 | | 155 | A DARK REDDISH MATERIAL IS COMING OVER |
| 240 | 290 (554°F) | 70 | 4 mm. | 165 | C U T I ( 123.3 g) |
| 260 | 310 / 312 °C. (590°/594°F.) | 70 | 4 | ABOUT 120 ml. PRODUCT COMING OVER | |

IT IS PLANNED TO PURIFY THIS PRODUCT FURTHER. (IT HAS NOW A FLAME POINT OF 240°C ....464°F)

SECTION E-3 .:USING DI-2-ETHYL HEXYL PHOSPHORIC ACID.

TABLE 140.

RESUMING REACTIONS BETWEEN ORGANO PHOSPHORIC ACIDS WITH TETRA ALKYL TITANATE

I. T 42- 75 . REACTING TETRA 2 ETHYL HEXYL TITANATE ( TOT) WITH

DI 2 ETHYL HEXYL PHOSPHORIC ACID

REPEAT OF T 42-65 OF TABLE 94 IN THE II.REPORT

USING 282 g. TOT WITH

322 g.ACID HEAT DEVELOPED ON MIXING

| TIME min. | TEMPERATURE C. | VARIAC # | PRESSURE mm. | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|
| - | 30°(86°F) | 45 | 2 -10 | - | BUBBLING |
| 20 | 90 (194°F) | 50 | | 5 | DISTILLATE CLEAR,COLORLESS |
| 40 | 100 | 50 | | 15 | |
| 80 | 103 (217°F) | 50 | | 25 | |
| 100 | 103 | 50 | | 35 | |
| 120 | 103 | 50 | | 55 | |
| 140 | 103 | 50 | | 75 | DISTILLATE MIGHT BE A |
| 160 | 103 | 50 | | 100 | 2 ETHYL HEXANOL MATERIAL |
| 180 | 103 | 50 | | 125 | |
| 200 | 103 | 50 | | 145 | |

II. T 42-73

FURTHER REACTING THE FLASK CONTENT WITH BASIC ZINC OCTOATE
IN A 1:1 RATIO INSTEAD OF THE 1:3 RATIO OF T 42-66 ( TABLE 94, II.REPORT)
USING 81.9 g.FLASK RESIDUE WITH
81.9 g. ZINC OCTOATE AND
0.5 g. Al $Cl_3$

N O HEAT ON MIXING

| | | | | | |
|---|---|---|---|---|---|
| - | 20 (68°F) | 45 | 2 -10 | - | BUBBLING GENTLY |
| 35 | 85 (185°F) | 50 | | A FEW | DROPS DISTILLATE |
| 60 | 85 | 50 | | 20 | CLEAR COLORLESS DISTILL. |
| 85 | 105 (221°F) | 55 | | 25 | |
| 100 | 155 (311°F) | 60 | | 40 | |
| 120 | 155 | 60 | | 55 | |
| | | | | | C U T I ( 36 g.) |
| 140 | 155 | 60 | | 20 | YELLOW IN COLOR |
| 180 | 155 | 60 | | 40 | |
| 200 | 155 | 60 | | 50 | |
| 210 | 155 | 60 | | 60 | |
| 230 | 155 | 60 | | 70 | |
| 240 | 155 | 60 | | 75 | |
| | | | | | C U T II. ( 52.8 g.) |

IN THIS 1:1 RATIO NO HIGH TEMPERATURE CUT WAS OBTAINED. THE FLASK CONTENT WAS COMPLETELY CHARRED.
IN THE 1:3 RATIO A CUT WAS OBTAINED BETWEEN 305°AND 320°C.( 580°F/ 608°F)

TABLE 141.

RESUMED STUDY OF THE REACTING PRODUCT BETWEEN TETRA OCTYL TITANATE AND DI 2 ETHYL HEXYL PHOSPHORIC ACID ( T 42-75) OF TABLE 140.

TEST T 42- 78 : USING 100 g. FLASK RESIDUE OF TEST T 42-75 WITH 200 g. BASIC ZINC OCTOATE R A T I O : 1 : 2

IN PRESENCE OF 0.5 g. ALUMINUM CHLORIDE CATALYST

NO HEAT ON MIXING.

| TIME min. | TEMPERATURE C. | VARIAC # | PRESSURE mm. | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|
| - | 24 °(75°F) | 50 | 2-10 | - | BUBBLING |
| 15 | 55 (131°F) | 50 | | 5 | CLEAR COLORLESS LIQUID |
| 20 | 55 | 50 | | 10 | |
| 30 | 55 | 50 | | 15 | |
| 45 | 80 (176°F) | 50 | | 20 | |
| 80 | 120 (248°F) | 50 | | 20 | |
| 95 | 140 (284°F) | 50 | | 25 | |
| | | | | | CUT I |
| 110 | 160 (320°F) | 60 | | 20 | YELLOW CLEAR DISTILLATE |
| | | | | | CUT II |
| 135 | 140 | 50 | | - | |
| 160 | 160 | 55 | | 25 | |
| 200 | 200 (392°F) | 65 | | 45 | |
| 245 | 250 (482°F) | 75 | | 55 | DISTILLATE DARKER |
| | | | | | CUT III |
| 270 | 265 (509°F) | 75 | | 15 | A DARKER MATERIAL |
| 280 | 200 (392°F) | 75 | | - | TEMPERATURE DROPPED AND THE POT CONTENT APPEARED TO DECOMPOSE. |

REVIEW: IN THE 1:1 RATIO OF TABLE 140 NO HIGH TEMPERATURE WAS OBTAINED.

IN THE 1:2 RATIO OF THIS TEST A SMALL YIELD OF HIGH TEMPERATURE CUT WAS OBTAINED.

IN THE 1:3 RATIO OF TABLE 94 (II. REPORT) A HIGHER YIELD OF HIGH TEMPERATURE CUT UP TO 320°C. ( 608°F)

TABLE 142

REACTING THE REACTION PRODUCT BETWEEN TETRA OCTYL TITANATE AND DI 2 ETHYL HEXYL P H O S P H O R I C A C I D ( T42-45) OF TABLE 140 AGAIN WITH BASIC ZINC OCTOATE IN THE RATIO OF 1 : 3 ( T 42- 84)

USED: 1 part by weight ( 150 g) T 42-75

3 parts by weight ZINC OCTOATE with 0.5 g ALUMINUM CHLORIDE.

| TIME min. | TEMPERATURE C. | VARIAC # | PRESSURE mm. | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|
| - | 27° (81°F) | 50 | 2-10 | - | BUBBLING |
| 30 | 30 (86°F) | 50 | | - | |
| 60 | 95 (203°F) | 55 | | 3 | CLEAR COLORLESS FLUID |
| 70 | 95 | 55 | | 20 | |
| 80 | 90 (194°F) | 55 | | 30 | |
| 110 | 98 (208°F) | 60 | | 40 | |
| 130 | 150 (302°F) | 60 | | 50 | WHITE FUMES |
| 140 | 155 (311°F) | 60 | | 60 | |
| | | | | | C U T I |
| 160 | 170 (338°F) | 60 | | 45 | SLIGHTLY YELLOW |
| 180 | 170 | 60 | | 80 | |
| 190 | 190 (374°F) | 60 | | 125 | |
| 210 | 185 (365°F) | 60 | | 165 | |
| 240 | 120 (248°F) | 65 | | 180 | |
| 260 | 175 (347°F) | 70 | | 190 | |
| 300 | 200 (392°F) | 70 | | 200 | |
| | | | | | C U T II ( 160 g.) |
| 310 | 220 (428°F) | 70 | | 20 | CLEAR YELLOW DISTILLATE |
| 340 | 245 (473°F) | 70 | | 40 | |
| 360 | 255 (491°F) | 70 | | 60 | |
| | | | | | C U T III |
| 380 | 300 (572°F) | 70 | | | A DARK VISCOUS PRODUCT IS COMING OVER |

PRODUCT ARRIVED BETWEEN 310 °AND 320 °C. (590° and 608°F.)

THIS PRODUCT WAS FURTHER MODIFIED WITH BENZYLALCOHOL IN TEST T 33 -89 AND THEN SUBJECTED TO AN OXIDATION RESISTANCE TEST ( TEST T 42- 87).

TABLE 143.

USING PHOSPHORUS PENTOXIDE IN A REACTION BETWEEN

DI 2 ETHYL HEXYL PHOSPHORIC ACID T 42- 106

USED: 166 g. DI 2 ETHYL HEXYL PHOSPHORIC ACID

71 g. TETRA ISOPROPYL TITANATE AND

0.5 g. PHOSPHORUS PENTOXIDE

BENZENE ADDED.

MUCH HEAT EVOLVED ON MIXING

| TIME min. | TEMPERATURE C. | VARIAC # | PRESSURE mm. | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|
| - | 25° (77°F) | 30 | ATM | 3 | CLEAR COLORLESS FLUID |
| 30 | 35 (95°F) | 40 | | 50 | |
| | | | | | CUT I |
| 60 | 75 (167°F) | 45 | 2 - 1 0 | 10 | CLEAR COLORLESS FLUID |
| | | | | | FLASK CONTENT VISCOUS |
| 90 | 78 (172°F) | 55 | | 20 | |
| 120 | 80 (176°F) | 55 | | 45 | |
| | | | | | CUT II |
| 160 | 170 (338°F) | 65 | | 5 | FOAMING IN THE FLASK |
| 170 | 100 | 40 | | 5 | |
| 200 | 125 (257°F) | 40 | | 10 | CLEAR DISTILLATE |
| 220 | 125 | 40 | | 20 | |
| 300 | 125 | 40 | | 70 | |

THE FLASK CONTENT WAS SOLID FOR THE LAST 30 MINUTES. . LOW TEMPERATURE CUT DISTILLATE CONTINUED TO COME OVER.

- - - -

TABLE 144.

MORE OXIDATION RESISTANCE TESTS

I. THE 1:1 ( BY WEIGHT) MIXTURE OF THE BENZYLALCOHOL MODIFICATION OF THE T42-80 TETRAISOPROPYL TITANATE / BASIC ZINC OCTOATE PRODUCT MADE WITH TITANIUM TETRA CHLORIDE AS CATALYST ( AND INHIBITED DOW SILICONE FLUID 5 2 0 PREPARED IN TABLE 100 OF THE II. REPORT.

USED 38.4 g INHIBITED SILICONE FLUID AND
38 4 g T 42-80

WEIGHT OF EMPTY FLASK ... 19^ 3 g WITH 243 g MIXTURE

MIXTURE ACTUALLY USED . 4^ 7 g

WITH ONE STRIP EACH OF COPPER, ALUMINUM AND STEEL AT 2 0 0 °CENTIGRADE ( 392°F) WITH 5 LITER AIR / HOUR ) VARIAC POSITION 45)

AFTER 72 HOURS DARKER IN COLOR , BUT STILL FLUID.

WEIGHT AFTER 72 HOURS ... 228 g. LOSS : 15%

II. THE BENZYLALCOHOL MODIFICATION ( T 33-89) OF THE REACTION PRODUCT T 42-84) OBTAINED FROM FIRST REACTION TETRA ISOPROPYL TITANATE WITH DI 2 ETHYL HEXYL PHOSPHORIC ACID ( T 42-75) AND THEN REACTING THIS PRODUCT WITH BASIC ZINC OCTOATE ( T 42-84)

WEIGHT OF SET UP BEFORE TEST . 21^ 1 g.

AFTER TEST . 210 .9 g.

PRODUCT T 33-89 USED ... 33.1 g. LOST 5.2 g. LOSS: 6 %

STEEL BEFORE TEST ..... 1.4207 g. AFTER TEST : 1.4209 g. LOSS ...-

COPPER BEFORE TEST. ..... 0.4320 g. AFTER TEST : 0.4318 g. LOSS:0.046%

ALUMINUM BEFORE TEST ..... 0.5361 g. AFTER TEST : 0.5365 g. LOSS.... -

SECTION F. THE INTRODUCTION OF CHLORINE GROUPS.

INTRODUCTION.

1. USING REACTIONS WITH 2-CHLOROETHANOL (TABLES 145-149)

The introduction of chlorine in these experimental materials was utilized by transesterifying the tetraisopropyl titanate with a halogenated alcohol, such as 2-chloro ethanol. TABLE 145 shows that such a transesterification takes place nearly quantitatively. This material was then complexed with zinc octoate instead of the halogen free titanate.

In TABLE 146 both reactions were carried out in one vacuum distillation. In TABLE 147 the earlier approach of TABLE 144 was taken up again. In none of these tests was it possible to obtain under vaquum the desired distillation fluid at a temperature range around 300°C. (572°F.). When the reaction product between the titanate and the zinc octoate was produced first ( with $TiCl_4$ as catalyst), and 157 g. of this product was reacted with chloroethanol, the 300°C. ( 572°F.) product was obtained. ( TABLE 148). That the material actually interreacted, and that the low cut in this Table did not represent a recovered chloroethanol, was seen in the fact that it had a different refractive index. This study was repeated in TABLE 149 and again the 300/310°C. (572°F.-590°F.) cut was obtained. That hereby the reaction flask material turned very dark in a different color than observed without the use of chloroalcohol is also to be observed. This study is being continued.

2. USING CHLORINE AND PHOSPHORUS IN THIS DI CHLORO PROPYL PHOSPHATE. ( TABLE 150).

A solid reaction product which forms no flame in contact with an open flame, was obtained by reacting tetraisopropyl titanate with a tris di chloro propyl phosphate, a commercial material offered as "FR-2". ( TABLE 150). This material represents an attempt to introduce phosphorus and chlorine simultaneously; but the fact that the reaction product is a solid, makes it not useful for this development. The work is to be continued with similar materials, to aim for a fluid titanium-oxygen and phosphorus and halogen product.

- - -

TABLE 145.

MODIFICATION OF THE TPT/ZINCOCTOATE COMPLEX MATTER

WITH 2 CHLOROETHANOL

I. REACTING TPT AND 2 CHLORETHANOL T 40-78

USED: 2 MOLES 2 CHLORETHANOL .... 161 g.

AND 1/2 MOLE TETRAISOPROPYL TITANATE ..... 142.5 g.

| TIME min. | VARIAC | PRESSURE mm. | TEMPERATURE C. | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|
| - | 30 | 3.5 | 37°(99°F) | - | ISOPROPANOL COMING OVER |
| 10 | | | 40 (104°) | 40 | |
| 20 | | | 40 | 80 | |
| 30 | | | 40 | 120 | |
| 35 | | | 60(140°F) | 120 | NO MORE FLUID COMING |

CUT I .... 107 g.
TRAPFLUID.. 19 g.
126 g.

THEORETICAL YIELD IN ISOPROPANOL .....120 g.
(PRODUCT HAS SLIGHT ODOR OF CHLOR ETHANOL )

NEW PRODUCT ASSUMED TO BE $Ti-\left(O-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{Cl}{CH}}\right)_4$ mol.wt.367 g.

THEORETICAL YIELD ... 183.5 g. ACTUAL YIELD .... 177 g.

II. REACTING THIS YIELDED MATERIAL ( 163 g) WITH

ZINC OCTOATE 22% Zn(378 g)

| | | | | | |
|---|---|---|---|---|---|
| - | 40 | 3.5 | 27°(81°F) | - | |
| 20 | | | 170 (338°F) | - | |
| 25 | | | 170 | 20 | CLEAR YELLOW LIQUID,ODOR |
| 50 | 50 | 3.5 | 170 | 150 | LIKE CHLOROETHANOL |
| 70 | 70 | 3.5 | 185(365°F) | 170 | |
| | | | | | CUT I |
| 90 | 70 | 3.5 | 60(140°F) | - | |
| 110 | 70 | 3.5 | 200(392°F) | - | |
| 115 | 70 | 3.5 | 280(536°F) | - | PRODUCT-LIKE MATERIAL APPEARS |
| 120 | 70 | 3.5 | 290(554°F) | 10 | |
| 140 | 70 | 3.5 | 290 | | EXTENSIVE DECOMPOSITION IN FLASK |

- - - -

TABLE 146.

MORE ATTEMPTS TO INTRODUCE A CHLORINE GROUP INTO THE TITANATE PRODUCT

III. T 38 - 76

FIRST ADDED 67.5 g.2 CHLOROETHANOL TO

72 g. TETRA ISOPROPYL TITANATE.

MIXTURE TURNED VERY HOT

HERE ADDED 190 g. ZINC OCTOATE ( NOT MUCH TEMPERATURE CHANGE)

AGAIN ADDED: 4.5 g. WATER MORE HEAT RELEASED

| TIME min. | TEMPERATURE C. | VARIAC | PRESSURE mm. | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|
| - | 27° (81°F) | 40 | 2-10 | - | |
| 30 | 35 (95°F) | 45 | | 5 | ASSUMED TO BE ISOPROPANOL |
| 40 | 40 (104°F) | 45 | | 15 | |
| 50 | 42 (108°F) | 45 | | 25 | |
| 60 | 38 (100°F) | 50 | | 33 | |
| | | | | | CUT I: 26 g. AND 15 g. IN TRAP |
| 66 | 65 (149°F) | 50 | | 5 | |
| 75 | 75 (167°F) | | | 20 | |
| 85 | 80 (176°F) | | | 25 | ASSUMED TO BE 2 CHLOROETHANOL |
| 90 | 82 (180°F) | | | 30 | |
| 100 | 84 (183°F) | | | 35 | |
| | | | | | CUT II 35 g. AND 5 g. IN TRAP |
| 120 | 110 (230°F) | 60 | | 5 | |
| 133 | 124 (255°F) | | | 15 | YELLOW LIQUID |
| 140 | 136 (277°F) | | | 20 | |
| 145 | 149 (300°F) | 65 | | 25 | |
| 150 | 172 (342°F) | 70 | | 30 | |
| 154 | 181 (358°F) | | | 35 | |
| | | | | | CUT III |
| 170 | 140 (284°F) | 70 | | - | |
| 180 | 110 (230°F) | | | - | |
| 195 | 210 (410°F) | 70 | | 5 | DARK BROWN ,SLIGHTLY VISCOUS |
| 208 | 208 (406°F) | | | 15 | |
| 210 | 205 (401°F) | | | 25 | |
| 220 | 180 (356°F) | | | 30 | |
| | | | | | C U T IV 30 g. BURNS ON END OF SPATULA IN OPEN BUNSEN BURNER |

FLASK CONTENT SOLIDIFIED INTO BROWN SOLID

TABLE 147.

ATTEMPTS TO INTRODUCE A CHLORINE GROUP INTO THE TITANATE

I. T 38- 72

REACTING TETRA ISOPROPYL TITANATE WITH 2 CHLOROETHANOL

1/2 mole
170 g.

$CH_2 - Cl$
$CH_2 - OH$

3/2 moles
144 g.

LARGE AMOUNT OF HEAT EVOLVED UPON MIXING

| TIME MIN. | TEMPERATURE C. | VARIAC | PRESSURE mm. | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|
| - | 24°(75°F) | 30 | ATM | - | |
| 40 | 82 (180°F) | 40 | | 10 | |
| 50 | 84 (183°F) | 45 | | 35 | |
| 62 | 86 (187°F) | 45 | | 60 | |
| 76 | 83(181°F) | 50 | | 85 | ASSUMED TO BE ISOPROPYL |
| 94 | 89 (192°F) | 50 | | 95 | ALCOHOL |
| 105 | 88 | 55 | | 110 | |
| 120 | 90 | 55 | | 120 | |
| 125 | 94 | 55 | | 125 | |
| 135 | 98 | 55 | | 130 | ml. CUT I .... 98 g. |

AS ALCOHOL IS BEING DRIVEN OFF THE REACTION MIXTURE TURNS DARKER

II. T 38-74

REACTING THE PRODUCT OF I. .... 88 g. WITH

ZINC OCTOATE.....190 g. IN PRESENCE OF 4.5 g. WATER

SLIGHT HEAT NOTED ON MIXING OF I. WITH ZINCOCTOATE AND MORE ON ADDING THE WATER

| | | | | | |
|---|---|---|---|---|---|
| - | 27°(81°F) | 40 | 2-10 | - | |
| 30 | 45 (113°F) | | | 10 | ODOR OF 2 CHLOROETHANOL |
| 60 | 50 (122°F) | | | 20 | |
| 70 | 58 (136°F) | 45 | | 25 | C U T I |
| 80 | 80 (176°F) | 50 | | 5 | |
| 90 | 100 | 60 | | 8 | CLEAR LIQUID SLIGHTLY |
| 110 | 100 | | | 13 | YELLOW |
| 120 | 100 | 65 | | 16 | C U T II |
| 140 | 180(356°F) | 70 | | 10 | |
| 150 | 185(365°F) | 75 | | 20 | ORANGE LIQUID |
| 160 | 190(374°F) | | | 30 | C U T III |
| 170 | 140(284°F) | 75 | | 5 | DARK BROWN CLOUDY LIQUID |
| 180 | 130(266°F) | 80 | | 10 | |

POT SOLIDIFIED
TO BE REPEATED

TABLE 148.

A MODIFICATION REACTION OF THE TETRA ISOPROPYL TITANATE/ZINCOCTOATE REACTION PRODUCT ( WITH $TiCl_4$ AS CATALYST ) USING 2 CHLOROETHANOL

I. APPROACH T 43 -1

USING 157 g. REACTION PRODUCT PREPARED AS T 42-95 ( TABLE 111).

60 g 2 CHLOROETHANOL

| TIME min. | TEMPERATURE C. | VARIAC # | PRESSURE mm. | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|
| - | 30 °(86°F) | 0 | 7 | - | - |
| 15 | 35 (95°F) | 40 | 7 | 10 | CLEAR COLORLESS FLUID |
| 25 | 33 (91°F) | | 7 | 35 | |
| 40 | 33 | | 7 | 45 | |
| 65 | 33 | | 7 | 55 | |
| 90 | 30 | | 6 | 55 | |
| | | | | | C U T I .... 44 g. |
| 120 | 55 (131°F) | 55 | 7 | - | |
| 145 | 87 (189°F) | | 7 | - | |
| 160 | 110 (230°F) | | 7 | - | |
| 175 | 133 (271°F) | | 5 | 2 | CLEAR YELLOW LIQUID |
| 190 | 155 (311°F) | 60 | 5 | 3 | |
| 230 | 146 (295 F) | 65 | 5 | 6 | |
| 325 | 75 (167°F) | | 5 | 8 | |
| | | | | | C U T II ..... 7.9 g. |
| 475 | 120 (248°F) | 70 | 6 | | SOME CLEAR YELLOW FLUID STARTS TO COME UP, BUT THE |
| 545 | 3 0 5 (581°F) | | 6 | | TEST SET UP DOES NOT GIVE HIGH ENOUGH |
| 575 | 290 (554°F) | | 6 | | TEMPERATURE TO COMPLETE THE DISTILLATION. |

COMPARISON OF THE REFRACTOVE INDICES:

| | | |
|---|---|---|
| 2 CHLOROETHANOL | $N_D^{24}$ ..... | 1.4380 |
| C U T I (ABOVE) | ..... | 1.4389 |
| C U T II (ABOVE) | ..... | 1 4459 |

TABLE 149.

MORE MODIFICATION TESTS FOR THE REACTION PRODUCT BETWEEN TETRAISOPROPYL TITANATE AND ZINCOCTOATE ( $TiCl_4$ CATALYST) WITH 2 CHLOROETHANOL

II. T 43- 4 USING 196 g. PRPDUCT T 43-2 ) AND

100 g. 2 CHLOROETHANOL

NO HEAT EVOLVED ON MIXING

DISTILLATION WITH CAPILLARY

| TIME min. | TEMPERATURE C. | VARIAC # | PRESSURE mm. | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|
| - | 28 °(83°F) | 45 | 2-10 | - | |
| 20 | 35 (95°F) | 50 | | 10 | CLEAR |
| 35 | 30 | | | 50 | LIGHT YELLOW |
| 45 | 30 | | | 70 | |
| 90 | 27 | | | 80 | |
| | | | | | CUT I |
| 120 | 162 (323°F) | 55 | | | - LIGHT YELLOW FLUID COMING |
| 135 | 143 (289°F) | | | 10 | |
| 195 | 70 (158°F) | | | 20 | |
| | | | | | CUT II |
| 215 | 43 (109°F) | 55 | | | - POT VERY DARK |
| 275 | 180 (356°F) | | | - | |
| 295 | 180 | | | | - (USING NOW ELECTRIC BANDHEATER |
| 325 | 180 | | | - | TO GET MATERIAL OVER) VARIAC 45 |
| 342 | 300(572°F) | 75 | 2- 10 | - | |
| 355 | 305(581°F) | 75 | | | PRODUCT COMING OVER |
| 365 | 310(590°F) | 75 | | | AS AN AMBER CLEAR FLUID |

FLASH POINT OF PRODUCT .... 285°C....545°F.

FLAME POINT OF PRODUCT .... 310°C.. 590°F.

III. T 43-6 R E DISTILLATION OF ABOVE PRODUCT.

SINCE THE PRODUCT TURNED CLOUDY UPON STANDING FOR A FEW DAYS, IT WAS WASHED WITH ACETONE AND BENZENE AND THE SOLVENT DISTILLED OFF AT ATMOSPHERIC PRESSURE.

THEN CONTINUED UNDER VACUUM

| | | | | | |
|---|---|---|---|---|---|
| - | 30°(86°F) | 50 | 2 -10 | - | |
| 20 | 35 (95°F) | 65 | | - | |
| 50 | 35 | 65 | | - | |
| 200 | 260(500°F) | 75 | | - | |
| 230 | 305(581°F) | 80 | | | 10 ml. CLEAR, LOW VISCOUS YELLOW |
| | | | | | MATERIAL CUT I |
| | 305 / 320 (581°/608°F.) | ..... | | | 75 ml. PRODUCT |

REMAINS CLEAR ON STANDING.

TABLE 150.

REACTING TETRA ISOPROPYL TITANATE WITH CHLORINE CONTAINING ORGANO PHOSPHATE

USING T R I S D I C H L O R O P R O P Y L P H O S P H A T E

" F R - 2 "

I. TEST T 42 - 93

USED 72 g. TETRA ISOPROPYL TITANATE

108 g. TRIS DICHLOROPROPYL PHOSPHATE

0.5 g ALUMINUM CHLORIDE CATALYST

N O HEAT ON MIXING. CLOUDY FLASK CONTAINER TURNS EVEN MORE CLOUDY ON ADDITION OF THE ALUMINUM CHLORIDE.

| TIME min. | TEMPERATURE C. | VARIAC # | PRESSURE mm. | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|
| - | 25° (77°F) | 40 | 2-10 | - | BOILING SLIGHTLY |
| 30 | 28 (82°F) | 40 | | - | " " |
| 40 | 50 (122°F) | | | - | " " |
| 60 | 110 (230°F) | | | - | BOILING MORE RAPIDLY. FLASK CONTENT NOW CLEAR |
| 120 | 150 (302°F) | | | 10 | CLEAR, SLIGHTLY YELLOW FLUID |
| 130 | 155 (311°F) | | | 15 | |
| 140 | 160 (320°F) | | | 35 | WHITE FUMES |
| 160 | 165 (329°F) | | | 40 | |
| 170 | 145 (293°F) | | | 75 | C U T I |
| 190 | 120 (248°F) | 40 | | 25 | DISTILLATE DARKER FLASK CONTENT DEEP VIOLET TURNS INTO A HARD, DRY MATTER. |

THIS DRY SOLID REACTION PRODUCT FORMS IN AN OPEN FLAME

N O F L A M E .

II. TEST T 42-93 : MIXED 72 g. TETRA ISOPROPYL TITANATE AND 108 g. TRIS DICHLOROPROPYL PHOSPHATE AND 0.5 g. ALUMINUM CHLORIDE I N 40 g. BENZENE

NO HEAT ON MIXING. NOT CLOUDY AS ABOVE.

| | | | | | |
|---|---|---|---|---|---|
| - | 27° (81°F) | 40 | ATM. | - | BOILING SLIGHTLY |
| 30 | 80 (176°F) | 60 | | 20 ml. | BENZENE COMING |
| 40 | 80 ° | | | 34 ml. | CUT I |
| 45 | 40 (104°F) | 40 | 2 - 1 0 | - | |
| 60 | 80 176°F) | | | - | |
| 100 | 100 | | | - | |
| 120 | 130 (266°F) | | | 5 ml. | CLEAR, SLIGHTLY YELLOW FLUID |
| 140 | 140 (284°F) | | | 15 | |
| 160 | 142 (288°F) | | | 25 | |
| 180 | 140 | | | 35 | |
| 200 | 130 | | | 60 | |
| 210 | 125 (257°F) | | | 80 | CUT II |
| 220 | 115 (239°F) | 40 | | 10 | DARKER DEEP VIOLET MATERIAL |

POT MATTER HAS NOT CHARRED WHEN DISTILLATION WAS HALTED, BUT ON COOLING TURNS INTO A HARD SOLID AGAIN .

## SECTION G. REACTING THE TITANATE/ZINC OCTOATE PRODUCT WITH TETRA BUTYL TIN.

### INTRODUCTION

In the preceding project the product obtained from tetra isopropyl titanate and basic zinc octoate was reacted with certain tetra alkyl silanes, and it produced a new product which had more desirable qualities than before. A larger sample of this new product, diluted with inhibited silicone fluid, was tested in the Philadelphia Naval Laboratory with interesting and desirable properties. This was reviewed on pages 1 and 2 of Report No. 2 of this project.

The tetra alkyl silane which had been used at that time was a di-n-dodecyl di-n-octyl silane, or a silane with two different alkyl groups, each alkyl group in two positions. ( Newer work which will be reported in the next report will review the effect of other silanes, having assymetrically selected alkyl groups.)

In the present study tetra alkyl tin was used instead of tetra alkyl silane. A commercially available tetra butyl tin was selected. First a complex fluid was carefully produced from 1/3 mole zinc octoate-22% and 1/2 mole tetra isopropyl titanate, with aluminum chloride as catalyst; and this product was obtained at a constant temperature of 295°C. (563°F.) at 2 mm. Hg. pressure.

Two hundred grams of this product was then further reacted with 60 g. tetra butyl tin in 60 g. benzene, and a reaction product came over under 2.5 mm. Hg. pressure at a temperature of 340°C. (644°F). This product appears very interesting and will be investigated further.

The material was studied by emission spectrographic analysis. Hereby the product of TABLE 151-I ( that means, before tin modification) was compared with the tin modification of TABLE 151-II. The report of the spectroscopist reads "Comparison of the samples indicates that the tin did enter the compound. The zinc lines were not affected but the titanium lines were suppressed considerably". The meaning of this observation is still to be studied.

TABLE 151.

THE I.PREPARATION OF A REACTION PRODUCT BETWEEN THE TETRA ISOPROPYL TITANATE-ZINC OCTOATE REACTION PRODUCT AND T E T R A  B U T Y L  T I N

I. PREPARATION OF THE TPT/ZINCOCTOATE PRODUCT WITH ALUMINUM CHLORIDE
T 40 - 74

USED 1/3 mole ( 378.4 g) ZINC OCTOATE 22% Zn
1/2 mole ( 142.6 g) TETRA ISOPROPYL TITANATE
0.5 g. ALUMINUM CHLORIDE

| TIME min. | PRESSURE mm. | VARIAC I II | TEMPERATURE C. | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|
| - | 2.5 | 60 -60 | 27 °(81°F) | -- | |
| 60 | 2.5 | 60-60 | 95 (203°F) | - | CLEAR YELLOW FLUID APPEARS |
| 80 | 2.5 | 60- 60 | 110 (230°F) | 40 | |
| 110 | 2.5 | 60-60 | 110 | 110 | |
| 130 | 2.5 | 60-60 | 110 | 160 | C U T I |
| 160 | 2.5 | 60-60 | 160 (320°F) | - | DARK YELLOW FLUID APPEARS |
| 170 | 2.5 | 60-60 | 180 (356°F) | 30 | FLUID IS REDDISH |
| 190 | 2.5 | 60-60 | 210 (410°F) | 45 | C U T II |
| 220 | 2.5 | 60-60 | 280 (536°F) | - | PRODUCT APPEARS |
| 230 | 2.5 | 60-60 | 295 (563°F) | 30 | CLEAR GOLDEN COLOR |
| 240 | 2.5 | 60-60 | 295 | 80 | |
| 250 | 2.5 | 60-60 | 295 | 95 | |
| 260 | 2.5 | 60-60 | 295 | 110 | |
| 280 | 2.5 | 70-70 | 295 | 150 | |
| 290 | 2.5 | 70-70 | 295 | 200 | |
| 320 | 2.5 | 70-70 | 295 | 300 ml. | |

YIELD ... 325 g. ABOUT 8 0 % YIELD AT CLOSE TEMPERATURE RANGE

II. REACTING 200 g. OF THIS PRODUCT WITH
60 g. TETRA BUTYL TIN IN
60 g. BENZENE
T 40-77

| TIME min. | VARIAC | PRESSURE mm. | TEMPERATURE C. | VOLUME ml. | REMARKS |
|---|---|---|---|---|---|
| - | 40 | 3.5 | 27 °(81°F) | - | |
| 10 | 70 | 3.5 | 37 (99°F) | - | CLEAR COLORLESS FLUID |
| 40 | 70 | 3.5 | 39 (102°F) | 50 | DISTILLS |
| 70 | 70 | 3.5 | 170 (338°F) | - | CLEAR COLORLESS FLUID |
| 90 | 70 | 3.5 | 170 | - | |
| 120 | 90 | 3.5 | 170 | - | TEMPERATURE BEGINS DROPPING |
| 140 | 90 | 3.5 | 45 (113°F) | 100 | AT THE TAIL END OF THIS CUT SOME YELLOW COLOR APPEARED RAPID RISE OF TEMPERATURE |
| 160 | 90 | 3.5 | 310 (590°F) | - | |
| 180 | 90 | 3.5 | 330 (626°F) | 30 | |
| 230 | 90 | 3.5 | 3 4 0 (644°F) | 120 | MOST OF THE PRODUCT CAME AT |
| | | | TOTAL YIELD | 148 g. | CONSTANT TEMPERATURE : 340°C (644°F.) |

## SECTION H. SOME MORE WORK ON THE INHIBITED SILICONE FLUID 510.

The work of TABLE 152 follows the same pattern as in TABLES 99/100 of the preceding Report No. 2; but here a new factor has been introduced: When the fluid came from the inhibition treatment with Cerium 2 ethyl hexanoate in a dark orange color and was filtered through a Linde Molecular Sieve , Type 13X Powder, it turned lighter in color. It was of interest, therefore, to know if this lighter color might be accompanied by a decrease in Cerium content.

For this reason the unfiltered material and the filtered material were submitted to an emission spectrometer test . (SpectroChem Laboratories, Inc., Franklin Lakes,N.J.) The report of the laboratory of November 9, 1962 reads as follows: "The intensity of the Cerium lines did not change by filtering the Silicone Fluid through the molecular sieve" .

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TABLE 152.

MORE STUDIES ON THE INHIBITING OF SILICONE FLUID 510

I. NEW PREPARATION OF THE CERIUM 2 ETHYL HEXANOATE. T 40 - 75

NEUTRALIZED 34.6 g. 2 ETHYLHEXANOIC ACID WITH NaOH ( 2 N).

DISSOLVED 21.92 g. CERIUM AMMONIUM NITRATE IN 95% ALCOHOL.

MIXED AND COLLECTED THE GREENISH PRECIPITATE.

DISSOLVED THIS PRECIPITATE IN A MIXTURE OF ETHYL ETHER AND BENZENE.

FILTERED THE SOLUTION AND EVPORATED THE SOLVENTS BY HEATING ON STEAM BATH.

DRIED THE GREEN CRYSTALS.

II. PREPARED THE INHIBITED SILICONE FLUID BY T 40-76

HEATING 1.6g 2-ETHYL HEXANOATE CERIUM SALT (PREPARED IN I )

12.8 g. COPPER INHIBITOR 65 DU PONT

800 g. SILICONE FLUID DOW 510 -50

HEATED AT 285 °C. (545°F.) UNDER AIRSTREAM OF 40 LITER / HOUR

4 x 24 HOURS.

THE FLUID IS DARK ORANGE IN COLOR.

WEIGHT LOSS: 83 g. OR 10.5 % WEIGHT LOSS DURING TREATMENT.

THE MATERIAL TURNED LIGHTER IN COLOR WHEN FILTERED THROUGH

LINDE MOLECULAR SIEVE TYPE 13 X POWDER.

REFRACTIVE INDICES: THE NOT INHIBITED FLUID ..... 1.4224

THE INHIBITED FLUID ..... 1.4224

THE FILTERED INHIBITED FLUID.. 1.4224.

AT 24 C.

FLASH POINT OF FLUID ... 340°C. ( 644°F).

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WORK SCHEDULED FOR THE NEXT REPORT PERIOD.

In the new work period the following subjects will be pursued:

1. Further studies on different experimental materials with respect to the rate of flashing and self extinguishing properties before sustained burning occurs.
2. Aiming to introduce additional groups to further delay the sustained burning, such as by introducing phosphorus derivatives.
3. As 2) but introducing halogen groups alone or together with phosphorus.
4. As 2) but introducing nitrogen groups alone or together with phosphorus, or phosphorus and halogen.
5. Reacting the titanate zinc octoate compound with tetra alkyl tin, or di alkyl di chloro tin, or similar products.
6. Similar as 5), but using borates.
7) Similar as 5), but using tetra alkyl silanes, in particular, unsymmetrical alkyl silane, or an aliphatic/aromatic silane.

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